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LEVELS OF POLYCHLORINATED DIBENZO-P-DIOXINS, POLYCHLORINATED DIBENZOFURANS AND DIOXIN-LIKE PCBS IN OILS COMMERCIALIZED IN COLOMBIA

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Introduction

Polychlorinated dibenzo-p-dioxins (PCDDs), polychlorinated dibenzofurans (PCDFs) and dioxin-like polychlorinated biphenyles (dl-PCBs) are commonly known as dioxins and are part of POPs which are internationally recognized by UNEP[1]. It is well accepted there are several routes for human exposition to dioxins such as ingestion, inhalation and dermal contact[2]. However, daily intake becomes the main route for dioxin furans and related compounds exposure. According to the literature, dioxins are present in foods that have high lipid content and are generally associated with foods of animal origin such as fish products, dairy products and meats[2,3]. In this sense, over recent decades there has been a notable promotion to control pollutants content in food in many countries; meanwhile efforts have been made to protect the consumer health.

Colombia has implemented control in some food in order to encourage the implementation of monitoring programs to evaluate the levels in food and to identify the possible contamination sources. As a strategy, Ministry of Health and Social Protection which is the entity responsible for monitoring has established regulations for fish products with both internal consumption and export. In addition, the Ministry has recently established maximum levels for dioxins and dl-PCBs in oils from animal and vegetable origin, but this legislation does not make a particular mention in fish oils[4]. Oils of vegetable and animal origin represent a high intake in the country, hence is important to study and determinate the PCDD/Fs and dl-PCBs contamination levels in this oil products. To our knowledge, studies based on PCDD/Fs and dl-PCBs analysis in food from Colombia have not been reported in the literature. Therefore, our study includes the determination of levels of PCDD/Fs and dl-PCBs in olive, soybean and fish oil consumed in Colombia. These results allow evaluating whether the levels of PCDD/Fs and dl-PCBs exceed the maximum permitted in oil samples according to the both Colombian and European regulations.

Materials and methods

Sample treatment

Olive and soybean vegetable oil and fish oil were purchased in a local supermarket in Medellín-Colombia, and they were stored in a refrigerator at 1-3°C. Soybean and fish oil were produced in Colombia whereas olive oil comes from Spain. Once at the Laboratory of Dioxins in Barcelona, analytical procedure follows the minimum requirements established in well accepted methods. In summary, an extraction to isolate the target compounds from the bulk, followed by a strict clean-up process and a final detection of the target compounds using mass spectrometry with isotopic dilution as quantification method was applied.

For each sample, an aliquot (10-20 g) of oil was spiked with known amounts of standard mixtures of ^{13}C-PCDD/Fs EPA-1613 LCS and dioxin-like ^{13}C-PCBs WP-LCS (Wellington Laboratories Inc., Canada). Next, oil samples were treated with two modified silica gel columns, one modified with sulfuric acid (44% w/w) and the other, modified with sodium hydroxide (33% w/w), for removing organic components, fat and other interfering compounds. Each column was eluted with n-hexane and was rotary concentrated for the next purification step. The clean-up was performed on the sequential arrays of open chromatographic multilayer silica, alumina and carbon as adsorbents. Two fractions of PCDD/Fs and dl-PCBs were obtained after passing the extracts trough

tandem column, of modified silica and alumina. Then, the extracts were purified using a carbon column. Finally, all fractions were rotary concentrated and transferred into vials and spiked with ^{13}C- PCDD/Fs EPA-1613 ISS and ^{13}C-PCBs WP-ISS standards for the analysis.

GC–MS Instrumentation

Samples were analyzed by High Resolution Gas Chromatography coupled to High Resolution Mass Spectrometry (HRGC-HRMS) on a Gas Chromatograph (Thermo Fisher Scientific, Milan, IT) using a 60 m x 0.25 mm i.d. x 0.25 μm film thickness DB-5ms fused silica column (J&W Scientific, CA, USA) coupled to a High Resolution Mass Spectrometer (DFS, Thermo Fisher Scientific, Bremen, Germany). Quantification of PCDD/Fs and dioxin-like PCBs was based upon relative response factors (or optionally average responses) in accordance to the isotopic dilution method[5,6]. Recovery percent of ^{13}C-labelled compounds was calculated from area comparison between LCS and ISS compounds. Toxic equivalents were determined using WHO-TEF-2005 factors.

Results and discussion

Total concentrations of PCDD/F and dl-PCB are given in Table 1. PCDD/Fs concentrations ranged from 2.87 to 13.2 pg g^{-1}. Soybean oil samples show highest levels of PCDD/Fs (13 pg g^{-1}) even though differences between both selecting samples (4.7 and 13 pg g-1 of fat, respectively) were observed. As expected, fish oils (7.72 and 8 pg g^{-1}) show also high levels of PCDD/Fs expressed as the sum of the 17 congeners. Finally, the levels of PCDD/Fs found for olive oil were lowest compared to the other samples studied in this work. Regarding the contribution PCDD/Fs, in most oil samples 2,3,7,8-substituted isomers with a high-chlorination degree were predominant, especially OCDD followed by 1234678-HpCDF, 1234789-HpCDF and OCDF, as shown in Figure 1(a).

In addition, concentrations of dioxin-like PCBs were measured also considered in this study (Table 1). In this case, fish oils show highest concentration levels of dl-PCBs (493 and 6828 pg g^{-1}, respectively) while soybean oil exhibits lowest levels (109.51 pg g^{-1} of sample). Regarding the contribution dioxin-like PCBs, mono ortho-PCBs congener show the most important contribution. PCB-118 presented a predominant content followed by congener PCB-105 in all samples. For instance, fish oil present a remarkable mono-ortho PCBs contribution ranged from 97% to 99%. Similar trend in dl-PCBs distribution in vegetable oil was shown, while fish oils exhibit slight differences in the distribution pattern. With respect non-ortho PCBs, PCB-77 present a significant participation in the total dl-PCBs while the remaining congeners show content below 1%. The significant contribution of mono-ortho PCB found in this study is contrary with data published by Bordajandi et al. for vegetable oil samples, which reported a remarkable content in non-ortho[7]. Despite of this, our results are in agreement with results reported by Olli et al. who found an important contribution related to mono-ortho dl-PCBs (88%) for fish oil[8].

Table 1 also shows the total WHO-TEQ$_{2005}$ values for PCDD/Fs, expressed in pg WHO-TEQ g^{-1} in the upper bound approach. Generally, the toxicity pattern was dominated by 2,3,7,8-TCDD and 1,2,3,7,8-PeCDD and to a lesser extent by 2,3,4,7,8-PeCDF. The higher chlorinated congeners, which exhibited the highest PCDD/F concentrations, did not account to a significant percentage to the WHO-TEQ content due to their relatively low WHO-TEF values. Fish oils present the highest PCDD/Fs WHO-TEQ values (1.0 and 1.4 pg WHO-TEQ PCDD/F g^{-1}) followed by soybean oil sample that shows value of 1.3 pg WHO-TEQ PCDD/F g^{-1}. Besides, vegetable oils show lowest levels which present similar values 0.24 and 0.25 WHO-TEQ PCDD/F g^{-1} for soybean and olive oil, respectively. Once again, when the dl-PCB WHO-TEQ values were added a PCDD/Fs values, fish oil exhibited the highest levels (4.0 pg WHO-TEQ sum of PCDD/F and dl-PCB g^{-1}). In addition, soybean and olive oils present the lowest levels WHO-TEQ, which show similar values 0.36 and 0.40 pg WHO-TEQ sum of PCDD/F and dl-PCB g^{-1}, respectively. These results are in agreement with reported by Abad et al. who analyzed olive oil samples from Spain and found low levels with a range of concentration ranging between 0.14 and 0.44 pg WHO-TEQ g^{-1} [9]. On the other hand, Olli et al. reported a contamination ranging from 12 and 22 pg WHO-TEQ PCDD/F and dl-PCBs g^{-1} of fat in fish oils from Norwegian Sea[8]. Therefore, WHO-TEQ levels of dioxins, furans and dl-PCBs for fish oils found in this work are below values reported by Olli et al, as mentioned previously[8].

Table 1. Total concentrations and WHO-TEQ values for PCDD/Fs and dl-PCBs in oils samples commercialized in Medellín-Colombia (expressed in pg g^{-1} of fat and pg WHO-TEQ_{2005} g^{-1})

Compound	*Soybean oil 1*	*Soybean oil 2*	*Olive oil*	*Fish oil 1*	*Fish oil 2*
∑ **PCDD/Fs**	4.71	13.2	2.87	7.72	8.0
WHO-TEQ (PCDD/Fs)	**0.24**	**1.3**	**0.25**	**1.4**	**1.0**
∑ non-ortho-PCBs	10.27	38.0	10.63	31.14	149.9
WHO-TEQ (non-orthoPCBs)	0.12	0.055	0.13	0.82	2.83
∑ Mono-ortho-PCBs	99.24	89.0	102.33	5462.23	6678.8
WHO-TEQ (Mono-orthoPCBs)	0.003	0.003	0.003	0.16	0.20
∑ PCBs	109.51	127.0	112.96	5493.37	6828.6
WHO-TEQ (PCBs)	**0.12**	**0.06**	**0.14**	**1.0**	**3.0**
WHO-TEQ (PCDD/Fs + PCBs)	**0.36**	**1.4**	**0.40**	**2.4**	**4.0**

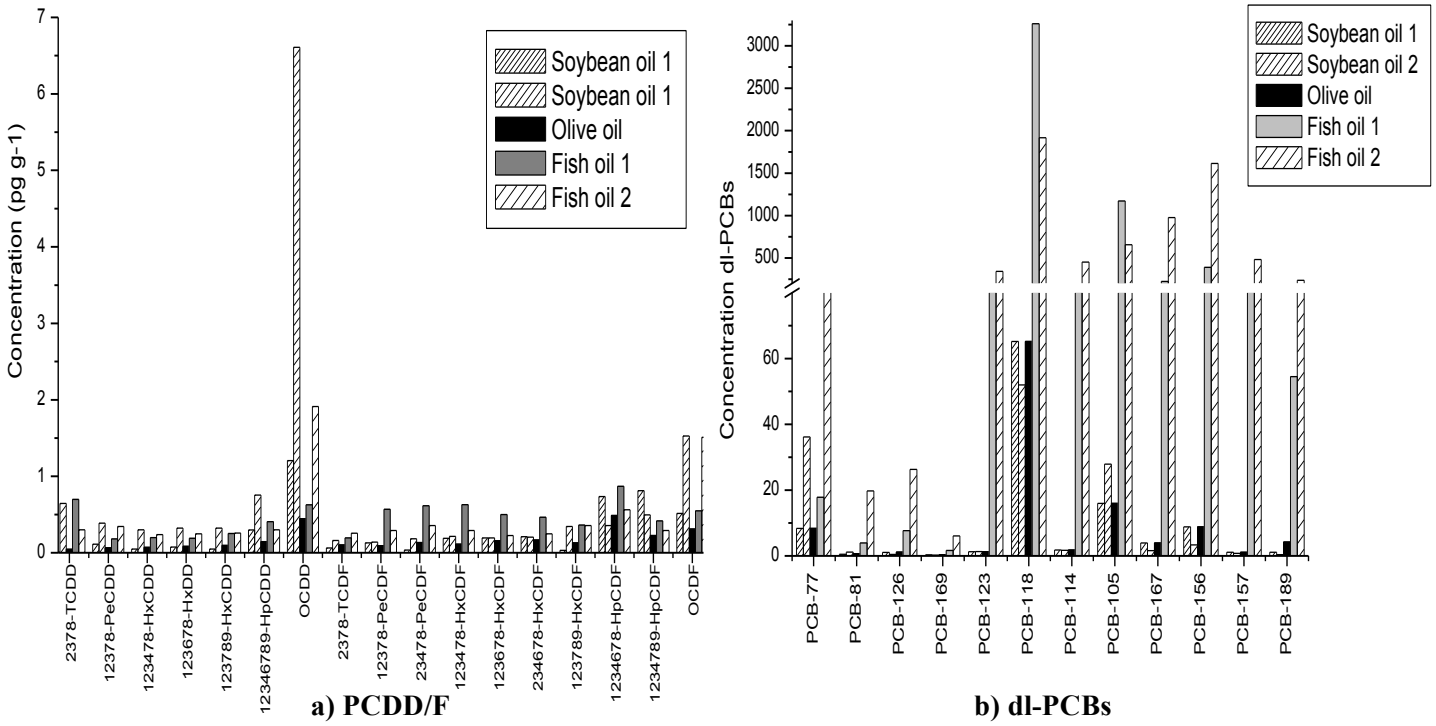

Figure 1. Concentrations of individual a) PCDD/Fs and b) dl-PCBs congeners in oil samples expressed in pg/g of fat

In the case of vegetable oil, levels found in this study are below the limits established by the Colombia legislation (vegetable oil and fat: 0.75 pg WHO-TEQ PCDD/F g^{-1} for PCDD/Fs and 1.5 pg WHO-TEQ TOTAL g^{-1} for PCDD/Fs and dl-PCBs)[4], except soybean oil sample (1.4 pg g^{-1} of fat) presented total PCDD/F and dl-PCBs concentrations above the maximum concentration levels established by this kind of oil products.

Regarding the fish oil, Colombian Regulation has established limits for PCDD/Fs and dl-PCBs content in oils and fats from terrestrial animal (bovine animals, sheep and pigs) but this legislation does not make a particular mention for fish oils. For this reason, it is not possible to evaluate the content of dioxins in this kind of oils from Colombian regulation. Despite of this, there are other legislations which define with certain specificity the maximum levels for oils and animal fats either marine or terrestrial (bovine, sheep, poultry and pigs). For instance, European Union regulation allows establishing comparison criteria about the maximum levels on the content of dioxins. In this sense, is possible affirm that fish oils show concentrations above the maximum concentration levels established by the EU (fish oil: 1.75 pg WHO-TEQ PCDD/F g^{-1} for PCDD/Fs and 6.0 pg WHO-TEQ TOTAL g^{-1} for PCDD/Fs and dl-PCBs)[10]. In addition, the level found for soybean oil (1.4 pg g^{-1} of fat) was slight higher than threshold established in Commission Regulation EU for vegetable oils (vegetable oil: 0.75 pg WHO-TEQ PCDD/F g^{-1} for PCDD/Fs and 1.25 pg WHO-TEQ TOTAL g^{-1} for PCDD/Fs and dl-PCBs)[10]. Therefore, results our study indicate that is necessary to encourage the implementation of monitoring programs in order to evaluate the PCDD/Fs and dl-PCBs levels in these kind of oils which are high consumption in the country.

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