Anthropogenic and Natural Polybrominated Diphenyl Ethers and Polychlorinated Biphenyls in Fish Oil Capsules from Different Countries.

Torres, FBM; Guida, Y; Alonso, MB; Meire, RO; Torres, JPM.

Radioisotopes Laboratory, Biophysics Institute, Federal University of Rio de Janeiro, Brazil, 21941-901.

Introduction

Eating fish is usually associated with good health and nutritional quality partially due to its omega-3 content, a polyunsaturated fat acid that is not synthetized by mammals [1]. Omega-3 is sold all around the world as nutraceutical supplements, generally a fish oil capsule to be ingested with meals. Fish or fish oil consumption is associated with reduced risk of heart diseases, strokes, hypertension, diabetes, arthritis, cancer, and improved vision, brain and reproductive function [2]. However, the presence of persistent organic pollutants (POPs) in fish raises the question of how beneficial it would be to consume fish oil capsules.

Polychlorinated biphenyls (PCBs) and anthropogenic produced polybrominated diphenyl ethers (PBDEs) are two examples of POPs. They are lipophilic, tending to accumulate in fat tissues. Both have been reported on marine organisms [3, 4]. Recently, the naturally produced methoxylated polybrominated diphenyl ethers (MeO-PBDEs) have been reported in marine food chains [4].

Based on the lipophilicity characteristics of select POPs, their presence in marine ecosystems and the capsule's lipid content, they are expected to be found in fish oil supplements. In fact, studies have shown the contamination of omega-3 capsules by several POPs [5-9]. Therefore, there is a need to evaluate the risks and benefits of consuming fish oil supplements and to monitor the concentrations of toxic chemicals that may be present in those capsules, as well as understanding the relationship between the omega-3 benefits and the harm caused by contaminants.

The aim of this study is to measure the concentration of PBDEs, MeO-PBDEs and PCBs in fish oil capsules from different countries.

Materials and methods

We sent an email message to the attendants of Dioxin 2015-São Paulo (Brazil) asking them to bring omega-3 fish oil capsules from their countries to the conference. In total, there were 17 samples from 10 different countries. Eleven samples were analyzed for PBDEs and MeO-BDEs (South Africa, Netherlands, USA, Japan, Australia, Brazil, China, Poland, Czech Republic, Germany and Portugal), while all 17 were analyzed for PCBs.

For each sample, three capsules were punctured with a needle and the oil content was placed in a 4 mL glass vial and homogenized. The procedure for oil clean up followed the one described by the FAO/SIDA Manual of Methods in Aquatic Environment Research [10]. The oil was dissolved in iso-octane (about 100 mg/mL) and then 1 mL of the dissolved solution was transferred to a glass tube containing 4 mL of concentrated sulfuric acid. The tube was closed and turned upside down 20 times and then centrifuged at 3400 RPM for 20 times. The dissolved extract was then transferred to a 2 mL glass vial and evaporated under a gentle nitrogen flow to dryness. 50 μL of tetrachloro-m-xylene (TCMX) at 100 ppb was added as internal standard.

The solution was then injected in a 7890 gas chromatograph coupled to a 5975C quadrupole mass spectrometer, both Agilent Technologies (Palo Alto, CA, USA). For PCBs quantification, analysis was performed on EI-SIM mode, using a HP-5ms 60 m x 0.25 mm x 0.25 μm chromatographic column. MeO-BDE and PBDE, were evaluated on NCI-SIM mode, using a DB-5ms 15 m x 0.25 mm x 0.25 μm chromatographic column. A matrix-matched calibration curve was used for quantification, with six points ranged from 5 ppb to 100 ppb. Limit of detection (LOD) was calculated based on the mean levels of five analytical blanks plus three times the standard deviation. For PBDEs, seven compounds were measured (BDE-28, BDE-47, BDE-100, BDE-99, BDE-154, BDE-153 and BDE-183). For MeO-BDEs, eight compounds were measured (6-MeOBDE-47, 2-MeOBDE-68, 5-MeOBDE-47, 4-MeOBDE-49, 5-MeOBDE-100, 4-MeOBDE-103, 5-MeOBDE-99 and 4-MeOBDE-101). In addition, for PCBs twenty eight congeners were measured, being and twelve dioxin-like (8, 18, 28, 52, 44, 66, 77, 81, 101, 103, 105, 114, 118, 123, 126, 128, 138, 153, 156, 167, 169, 170, 180, 189, 195, 198, 206 and 209).

Results and discussion

The results are presented in table 1. MeO-BDEs were found in all samples, mostly the 6-MeOBDE-47 and 2-MeOBDE-68. Fish oil concentrations of ΣMeO-BDE showed high variation values, ranging from 18 $ng.g^{-1}$ (Portugal) to 2262 $ng.g^{-1}$ (USA). In five samples, PBDEs were below LOD. When above LOD, fish oil concentrations of ΣPBDEs ranged from 5.8 $ng.g^{-1}$ (Germany) to 159.5 $ng.g^{-1}$ (USA). BDE-47 and BDE-153 were the most frequently detected.

For PCBs, in seven samples all levels were below the LOD. Values for the sum of concentrations of total PCBs when above LOD ranged from 5.8 $ng.g^{-1}$ (Poland) to 349.3 $ng.g^{-1}$ (USA). For dioxin-like PCBs (dl-PCBs), TEFs from Van den Berg et al, 2006 [11] were used. In only eight samples dl-PCBs were detected, the highest value was 1300 pg $TEQ.g^{-1}$ (UK) and the lowest value was 0.243 pg $TEQ.g^{-1}$ (Germany). For samples below LOD, TEQ values were counted as zero.

Alonso, 2014 [4] and co-workers suggest that concentrations of PBDEs are higher than those of MeO-BDEs in the northern hemisphere while the southern hemisphere have higher concentrations of MeO-BDEs over PBDEs based on levels found in cetaceans. Only the sample from Japan shows this trend in this study. The cited authors [4] also suggest higher concentrations of PBDEs in northern Atlantic sea then in the south Atlantic. We found higher levels of PBDEs in the USA sample than from Brazilian fish oil. However, low levels were found in fish oil Portugal. It is possible that the fish oil sold in one country comes from several other regions worldwide, since there is a lack of labelled information on where the fishes were caught.

Many products claim to be PCB free and in seven samples the levels were below the limit of detection. We compared the dl-PCBs values to the tolerable daily intake (TDI) proposed by JECFA 2001 [12] for dioxins, 2 pg TEQ/kg BW/day. A value of 70 kg was used for body weight and the number of capsules to be taken daily was based on label directions. Only two samples were above the TDI value, Poland 1 (2.9 pg TEQ/kg BW/day) and UK (55.7 pg TEQ/kg BW/day) fish oils, which may represent a significant threat to consumer´s health.

The high range between levels of all contaminants suggests that fish oil capsules contamination should be monitored. Similarly, Rawn et al [5] found a high range for organochlorine pesticides in Canadian fish oil supplements.

The lack of information from what kind of fish comes the oil and where it was caught does not contribute to the comprehension of the data, emails were sent to three sampled companies but none returned to date.

Omega-3 supplements health benefits are numerous but it may also serve as a route for POPs contamination. Ingesting low doses of POPs for a long time can result in chronic effects, consumers must be aware of contaminants levels in the products they buy.

Table 1: Contaminants levels in 1 g of fish oil. ("-"indicates that the sample was not analyzed for this compound).

Sample	Σ MeO-BDE ($ng.g^{-1}$)	Σ PBDE ($ng.g^{-1}$)	Σ PCB ($ng.g^{-1}$)	Σ dl-PCB (pg TEQ. g^{-1})
Australia 1	30.1	83.3	28.1	4.4
Australia 2	-	-	< LOD	< LOD
Brazil	20.8	< LOD	< LOD	< LOD
Canada	-	-	< LOD	< LOD
China	81	< LOD	< LOD	< LOD
Czech Republic	35.6	< LOD	12.8	57.3
Germany 1	108.7	5.8	10.1	0.2
Germany 2	-	-	< LOD	< LOD
Germany 3	-	-	31	0.9
Japan	34.5	84.1	< LOD	< LOD
Netherlands	223.2	54.3	349.3	0.4
Poland 1	388.6	< LOD	5.8	102
Poland 2	-	-	< LOD	< LOD
Portugal	18	< LOD	14.6	< LOD
South Africa	73.8	7.7	19.7	1.4
United Kingdom	-	-	13	1300
USA	2262	159.5	112.2	< LOD

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