DETERMINATION OF POPs (PCDD/F, DIOXIN-LIKE PCBs, MARKER PCBs, PBDEs AND OCP) IN HEALTH SUPPLEMENTS.

Martí M; Ortiz X; Martí R, Montaña MJ, Gasser M, Díaz-Ferrero J

Environmental Laboratory, Institut Químic de Sarrià (URL), Via Augusta 390 08017 Barcelona, Spain.
(jordi.diaz@iqs.edu)

INTRODUCTION

Last years, consumption of health or nutritional supplements has increased in our society. They are recommended as a supplement for the diet because of their mineral, vitamin, omega 3 and omega 6 fatty acid contribution, etc. A lot of these supplements contain oils among their components (fish oils or vegetable oils), especially those recommended for their omega 3/omega 6 content. Due to their persistence and lipophilic characteristics, polychlorinated dibenzo-p-dioxins (PCDDs), polychlorinated dibenzofurans (PCDFs), dioxin-like PCBs, marker PCBs, polybrominated diphenyl ethers (PBDEs), and organochlorine pesticides (OCP) bioaccumulate in fat tissues, especially in those animals, as fish, which show low metabolisation ability. Therefore, the consumption of nutritional supplements with oil components can increase the intake of POPs through the diet. The aim of this study is to analyse some of these encapsulated health supplements to determinate their POPs levels and if there are differences in their level related to the main components present in the supplement.

METHODS AND MATERIALS

Samples analyzed

Samples analyzed were 15 health supplements which contained different components, especially oily ones (from fish and from vegetable origin), collected from drugstores and dietetics stores. Table 1 shows sample codes and some of their characteristics.

Table 1. Codes and characteristics of samples analyzed.

Sample code	Main components		Sample code	Main components
F1	Fish oil		FV2	Fish oil + evening primrose oil
F2	Fish oil		V1	Pumpkin seed oil
F3	Fish oil		V2	Evening primrose oil
F4	Fish oil + mineral + vitamins (prescribed for pregnant women)		V3	Vegetable oil rich in omega 6
F5	Fish oil + mineral + vitamins (prescribed for pregnant women)		V4	Evening primrose oil
F6	Fish oil (cod liver oil)		V5	Evening primrose oil
F7	Fish oil (cod liver oil)		M1	Selenium, zinc and vitamin A, B6, C and E
FV1	Fish oil + flax seed oil			

Analytical method

Determination of PCDD/Fs, PCBs (marker and dioxin-like), HCB, ΣDDT and PBDEs were performed following an analytical method based on international norms (USEPA 1613 and USEPA 1614-draft) and related European Directives[1]. The main steps of the method are the following:

- Extraction of the oil from the capsules.
- Sample weighing (6 g).
- Addition of extraction internal standards labelled with ^{13}C to the sample.
- Oil solution in hexane
- Clean-up in multilayer silica column.
- Instrumental determination of marker PCB, HCB and ΣDDT by HRGC-μECD
- Fractionation of PBDE, dioxin-like PCBs and PCDD/Fs by HPLC equipped with a pyrenyl column.
- Concentration of each fraction under nitrogen stream and addition of syringe standards.
- Instrumental determination of DL-PCBs, PCDD/Fs and PBDEs by HRGC-HRMS and quantitation by the isotopic dilution method.

RESULTS AND DISCUSSION

Table 2 shows the total concentration of each family studied for the nutritional supplements analyzed.

Table 2. Total concentration of PCDD/Fs, DL-PCBs, marker PCBs, PBDEs, HCB and ΣDDT in the health supplements analyzed.

Sample code	PCDD/Fs (pg WHO-TEQ/g)	Dioxin-like PCBs (pg WHO-TEQ/g)	Marker PCBs (ng/g)	PBDEs (ng/g)	HCB (ng/g)	ΣDDT (ng/g)
F1	0.63	1.39	7.21	0.75	0.90	13.2
F2	0.29	0.88	15.6	1.20	0.19	25.1
F3	0.52	0.92	3.05	1.79	<LD	13.3
F4	1.26	0.29	0.14	0.47	<LD	1.47
F5	0.60	1.17	3.17	1.75	0.15	4.00
F6	0.90	12.1	98.3	18.2	17.8	184
F7	2.40	8.51	49.7	8.86	12.5	68.6
FV1	0.34	0.43	1.22	0.25	<LD	2.33
FV2	0.33	0.39	2.81	0.61	0.74	6.86
V1	n.d.	0.02	0.44	0.08	4.48	0.95
V2	0.18	0.03	1.20	2.14	0.77	1.43
V3	0.18	0.02	1.02	1.39	0.12	0.69
V4	0.16	0.03	1.62	n.d.	0.40	1.09
V5	0.20	0.05	1.11	1.88	3.85	2.01
M1	0.04	0.01	0.48	0.36	0.02	0.69

nd: not determined.

Levels of POPs detected in the supplements studied were comparable to those found in literature[2-4]. PCDD/F and DL-PCB concentrations were below the maximum levels established by EU Regulation[5] for most samples. Only two samples showed higher concentrations: F6 exceeded maximum level of PCDD/F+DL-PCB due to high concentrations of DL-PCB (12.1 pg TEQ/g) and F7 exceeded both maximum level of PCDD/F (2.40 pg

TEWQ/g) and maximum level of PCDD/F+DL-PCB. The main component of both supplements was fish oil, specified as cod liver oil.

In figure 1, range and median values of PCDD/F, DL-PCB, marker PCB and PBDEs in complements with different types of oil are compared.

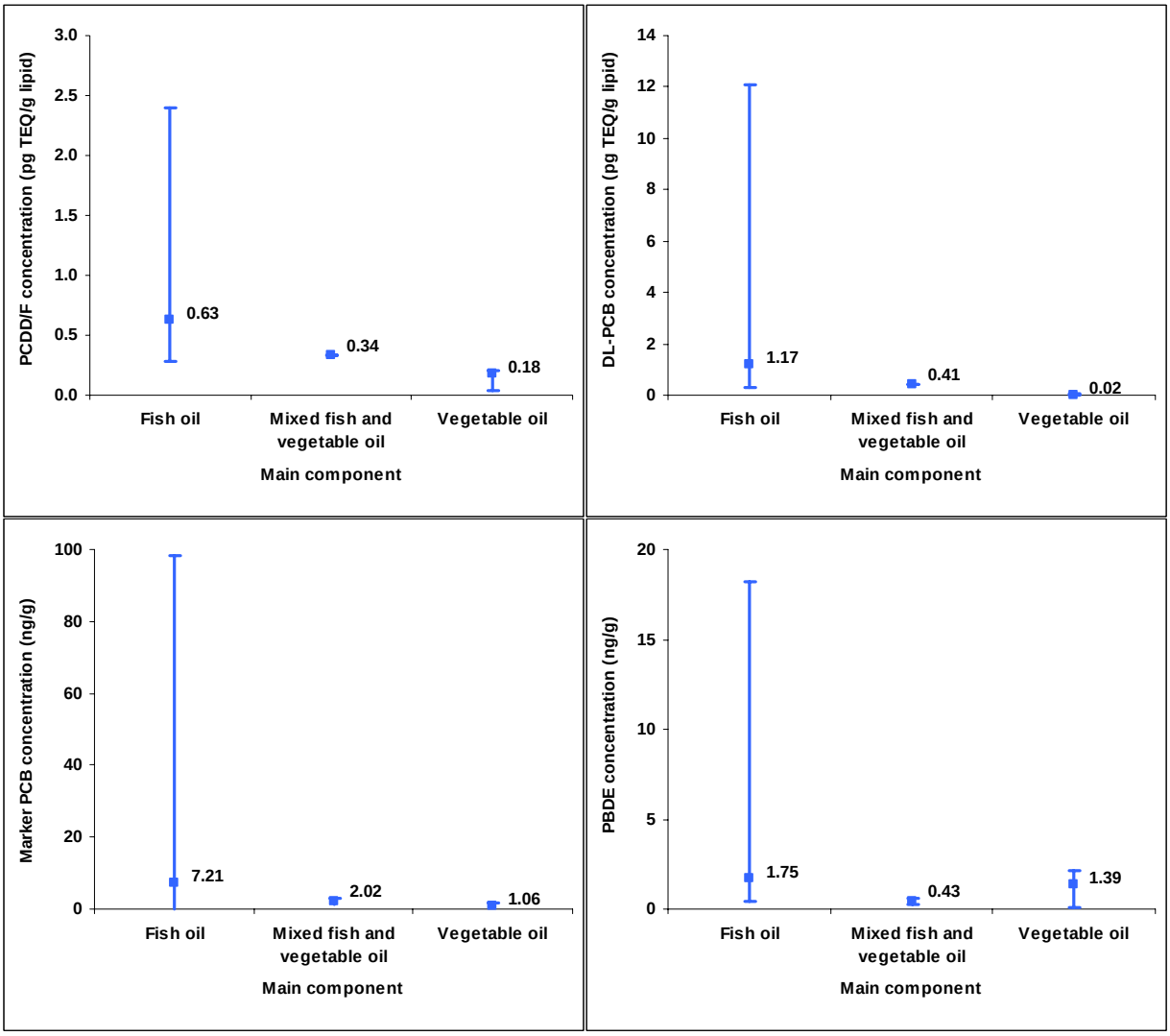

***Figure 1**. Comparison of PCDD/F, DL-PCB, marker PCB and PBDE concentrations for each group of supplement.*

Supplements based on fish oil showed higher variation in the level of POPs than those based on vegetable oils. For PCDD/F, DL-PCB and marker PCB, median concentrations were higher for fish oil-based supplements than for vegetable ones (between 3.5 and 45 times higher, depending on the analyte). However, for PBDE median values were similar: 1.75 ng/g for fish oil and 1.39 ng/g for vegetable oil. The mineral supplement analyzed presented POPs concentrations even lower than vegetable oil based supplements.

PCDD/F profiles in most samples were characterized by high chlorinated dioxins (HpCDD and OCDD) and variable amount of low chlorinated furans (TCDF and PeCDF). Only sample F4 showed a different profile with higher proportion of HxCDF, HpCDF and OCDF.

Dioxin-like PCB profiles were dominated by PCB 118, PCB 105, followed by PCB 156 and PCB 167. However, in most samples, especially those based on fish oil, PCB 126 was the most important contributor to TEQ concentration. Contribution of DL-PCB to total TEQ concentration was very high in fish oil-based supplements (50%-90%) while in those based on vegetable oil was quite low (10-20%).

Marker PCB profiles were different depending on the main component in the supplement. Figure 2 show the profiles of samples F6 and V4.

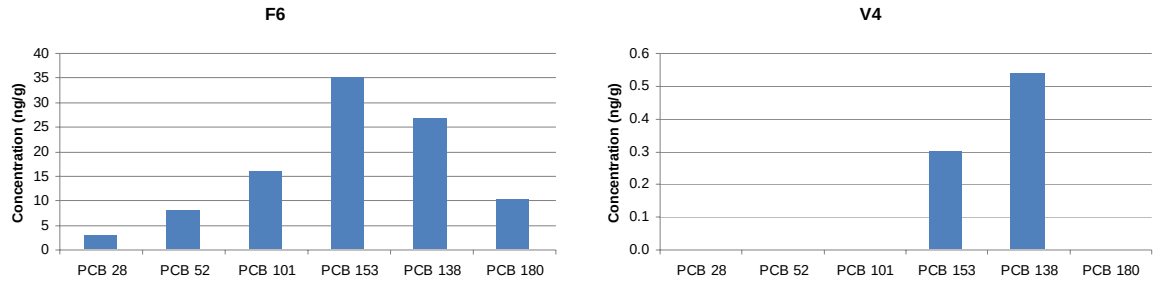

Figure 2. *Marker PCB profiles of samples F6 (based on cod liver oil) and for sample V4 (based on evening primrose oil).*

PBDEs profiles were different depending on the main component in the supplement. In those based on fish oil, BDE-47 was the most important congener followed by BDE-99 and BDE-100. In vegetable oil based supplements, BDE-209 was the most concentrated congener.

ACKNOWLEDGEMENTS

This work has been supported by the Spanish Ministerio de Educación y Ciencia (AGL2006-12235/ALI).

REFERENCES

1. Commission Regulation (EC) nº 1883/2006.
2. Hasegawa J., Guruge K.S., Nobuyasu S., Shirai Y., Yamata T., Nakamura M., Handa H., Yamanaka N., Miyazaki S. *Chemosphere* 2007; 69:1188.
3. Covaci A., Voorspoels S., Vetter W., Gelbin A., Jorens P.G., Blust R., Neels H. *Environ. Sci. Technol.* 2007 ; 41:5237.
4. Jacabos M.N., Covaci A., Gheorghe A., Schepens P. *J. Agric. Food Chem.* 2004; 52:1780.
5. Commission Regulation (EC) nº 1881/2006.