PBDDs, PBDFs AND PBBs IN SELECTED COD (Gadus morhua) LIVER PRODUCTS FROM 1972 - 2017

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Introduction: The observed trend in the occurrence of some chlorinated and brominated POPs including polychlorinated dibenzo-p-dioxins and furans (PCDD/Fs), polybrominated diphenylethers (PBDEs) and polychlorinated biphenyls (PCBs) in the global environment and foods over the last 2-3 decades, indicates a decline as a result of regulation and cleaner waste disposal technologies. However, the rates of decline for PCDD/Fs and PCBs for the regions of the Baltic Sea still appear to be rather low. A retrospective analysis of a number of historical medicinal grade cod-liver oils purchased in Northern and Central Europe during 1972 – 2001 revealed high contamination with PCNs, PCDD/Fs and PCBs and elevated contents of PBDEs[1,2]. Substantial quantities of these contaminants have also been observed in recently purchased (2017, from Polish markets) canned cod liver products used as food ("Cod liver in its oil" and "Pate of cod livers and vegetables")[1,2]. This study investigated the co-occurrence of other brominated POPs such as polybrominated biphenyls (PBBs) and polybrominated dibenzo-p-dioxins and furans (PBDD/Fs) in these products, sourced from the Baltic Sea and North Atlantic.

Materials and Methods: Cod liver oils of medical grade were either purchased directly from retail outlets, obtained from processing plants or were gifted by international organisations during the period 1972 to 2001. These were stored refrigerated in the original commercial containers or dark bottles. Canned cod livers were purchased as food products[1,2] just prior to beginning of the study in 2017.

The following compounds were analysed:

PBBs - IUPAC numbers #49, 52, 77, 80, 101, 126, 153, 169 and 209;

PBDDs - 237-TriBDD, 2378-TetraBDD, 12378-PentaBDD, 123478/123678-HexaBDDs and 123789-HexaBDD; PBDFs - 238-TriBDF, 2378-TetraBDF, 12378-PentaBDF, 23478-PentaBDF, 123478-HexaBDF and 1234678-HeptaBDF.

Sample aliquots were fortified with $^{13}C_{12}$-labelled internal standards and extracted by cold solvent extraction using a dichloromethane:hexane (40:60) mixture as described earlier[3,4]. The *ortho*-substituted PBBs were fractionated from non-*ortho* PBBs and PBDD/Fs using activated carbon. The two fractions obtained were further purified using activated alumina. Analytical measurements were carried out using HRGC-HRMS (Waters Autospec Ultima instrument fitted with a Hewlett Packard 6890N gas chromatograph)[3]. The analytical recoveries, precision (RSD) and detection limits (LOD) of the method (lipid weight) based on the use of $^{13}C_{12}$ labelled surrogates were typically in the ranges: 50–100%, 10% and 0.002-0.08 ng g^{-1} respectively for *ortho*-substituted PBBs, and 50–90%, 20% and 0.01–0.2 pg g^{-1} (PBDD/Fs and non-*ortho*-PBBs). Other quality control criteria used were similar to regulated PCDD/F and PCB measurements with the inclusion of in-house reference materials and method blanks which were evaluated prior to quantitation and reporting[4].

Results: The *ortho*-PBBs #49, 52, 101 and 153 occurred in all cod liver oils sampled and concentrations were in the ranges, 301 - 457, 71 - 390, 79 - 194 and 122 – 618 (pg g^{-1} fat), respectively. The canned cod liver products contained these contaminants in the ranges, 37 - 116 (#49), 46 - 112 (#52), 3 - 5 (#101) and 6 - 7 (#153) (pg g^{-1} whole weight). From the remaining *ortho*-PBBs tested, #80 and #209 were less frequently detected and levels were respectively up to 13 and 28 pg g^{-1} fat. Of the non-*ortho* PBBs, #126 and #169 were not detected and #77 was in the ranges 0.6-5.78 pg g^{-1} fat in oils and 0.06-0.126 pg g^{-1} whole weight in canned livers. The relative concentrations of the measured PBB congeners are shown in Figure 1. The data compiled suggests that PBB levels in cod liver oils showed peak values at the turn of the century, in 2001. Concentrations for the Baltic Sea and the North Atlantic fishing regions in Norway and Iceland showed similar levels during the period from 1972 -1993. These concentrations are consistent with the lower use of PBBs in these regions as compared to PBDEs, which showed considerably higher concentrations for the same samples[2].

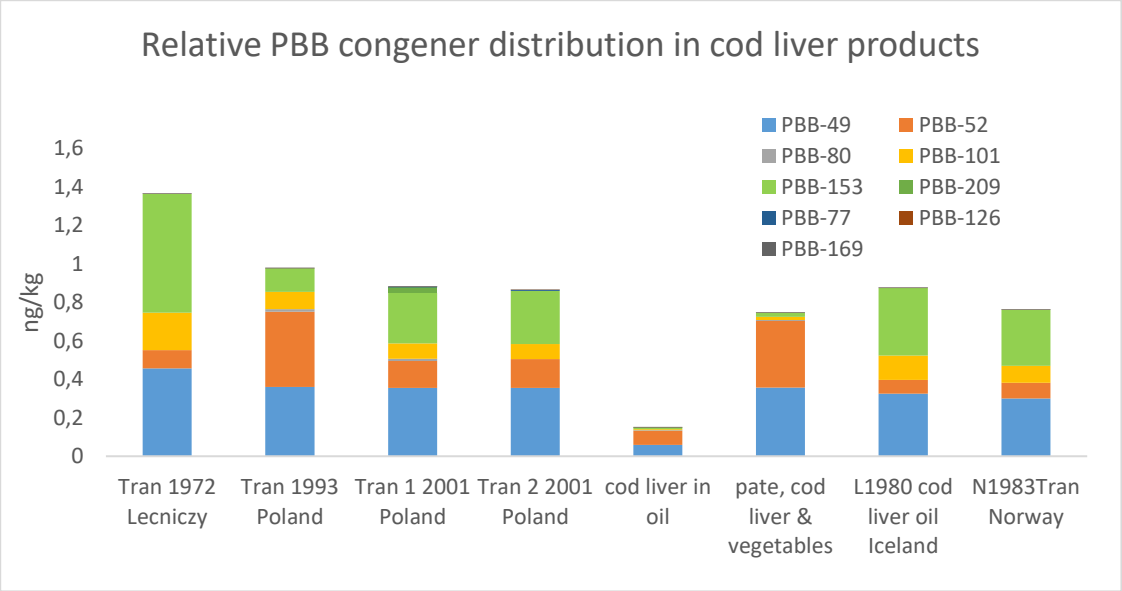

Figure 1. The relative distribution of PBB congeners in cod liver products from the Baltic Sea and North Atlantic.

The detection of PBDD congeners was infrequent with some congeners such as the 2378-TetraBDD and 12378-PentaBDD occurring only in the canned liver products. As observed in other studies[4,5], PBDFs occurred more frequently than PBDDs. 238-TriBDF was found in all samples; cod liver oils (0.573-5.249 pg g^{-1} fat) and canned livers (0.082-0.398 pg g^{-1} whole weight). 1234678-HeptaBDF was found in all of the Baltic Sea origin cod liver oils (0.055-0.302 pg g^{-1} fat) and in both of the canned liver products (0.073-0.086 pg g^{-1} whole weight), but was not detected in the North Atlantic oils. As observed in other studies on marine fish[6], these concentrations were relatively low in comparison to PCDD/Fs.

Conclusions: PBBs were detected in all samples, with concentrations appearing to peak in 2001. The concentrations of PBDD/Fs, *ortho*-PBBs and non-*ortho*-PBBs both in historical samples of cod liver oils and recently manufactured canned cod liver products were low.

References:

1. Falandysz J, Smith F, Panton S, Fernandes AR (2019) *Chemosphere* 231: 240-248.
2. Falandysz J, Smith F, Steel Z, Fernandes AR (2019) *Chemosphere* 232: in press.
3. Fernandes, A., White, S., D'Silva, K., Rose, M., (2004) Talanta, 63, 1147-1155.
4. Fernandes, A., Dicks, P., Mortimer, D., et al., 2008. Mol. Nutr. Food Res. 52, 238-249.
5. Fernandes A, Tlustos C, Smith F, Carr M, Petch R, Rose M (2009) *Food Add. Contam. Part B* 2: 86-94.
6. Fernandes, A., Mortimer, D., Holmes, Smith F, Panton S, et al., 2018. Env. Int., 114, 219-230.