Polychlorinated naphthalenes (PCNs) in Cod Liver Oil and Cod Liver Products Sourced from the Baltic Sea and the North Atlantic Ocean

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Introduction:

Polychlorinated naphthalenes (chloronaphthalenes, PCNs) were industrial chemicals widely used in the 20th century. This class of chlorinated aromatics has similar physico-chemical properties and very similar industrial applications as polychlorinated biphenyls (PCBs) and additionally they were also used as flame retardants. Environmentally, PCNs also demonstrate properties of persistence and high bioaccumulation potential, coupled with a similarity in structural configuration to PCDD/Fs (dioxins). PCNs are recognised as persistent organic pollutants (POPs), and are listed in Annex A and Annex C of the Stockholm Convention. Many congeners have also been reported to contribute to dioxin-like toxicity[1,2] eliciting a range of toxic responses such as mortality, hepatotoxicity, teratogenicity and carcinogenicity, although not all can be attributed to a dioxin-like pathway[3,4].

Although widely manufactured as technical grade commercial PCN mixtures for industrial and consumer use, all 75 PCN congeners can also be produced in certain high temperature processes (combustion, smelting etc.), and as significant unintentional impurities in chemical products[5]. Many of these congeners have been shown to accumulate and bio-magnify in aquatic food chains[6]. Earlier reports[7,8] show widespread occurrence in foods and a recent review of their occurrence in human tissue and foods[2] shows higher occurrence levels in fish relative to other foods.

In earlier studies, several POPs such as hexachlorobenzene, hexachlorocyclohexanes, chlordanes (CHLs), cyclodiene insecticides (Aldrin, Dieldrin), DDT and metabolites and polychlorinated biphenyls (PCBs) were reported as common contaminants of canned cod (*Gadus morhua*) livers and the more widely used product - cod-liver oils. Among these contaminants, DDT/metabolites and PCBs in particular, were found to dominate the occurrence[9-12]. Crude (unpurified) cod-liver oil that was sold in the past for medicinal and dietary supplement use could also be contaminated with other highly toxic POPs such as PCDD/Fs or PCNs but there was very little good quality data available in the literature on the occurrence of the latter in cod liver oil or cod liver. In this study, cod-liver oils produced as medicinal and dietary supplements in Iceland, Norway and Poland and available in the past (1972-2001) from European markets, capsuled cod-liver oil retailed in 2017 and varieties of canned liver products such as "Cod livers in cod liver oil" and "Pate - cod livers and vegetables" - produced in February 2017 from Baltic Sea cod livers and retailed in Poland have been examined for the occurrence of PCNs using highly selective and validated methods for food analysis[7].

Materials and Methods:

Cod-liver oils of medical grade sourced from the Baltic Sea or the North Atlantic and cod liver food products from the Baltic Sea were obtained as follows:

- Purchased in pharmacy shops in Gdańsk, Poland (1972– in original containers), or obtained from a processing plant in Gdynia, Poland (1993 and 2001),
- Donated by Red Cross (1980; L. cod-liver oil – original can),
- Purchased in a pharmacy shop in Norway (1983; M. T. – original bottle),
- Commercial cod-liver oil supplement bought in Poland (S. cod-liver oil in capsules – original jar bought from a commercial supplier S. Polska in 2017), and
- Two types of canned cod-liver products: "*Wątróbki rybne w tłuszczu własnym*" and "*Pasztet z wątróbek dorszowych*" produced in Łeba (Poland) in 2017.

The following PCN congeners were analysed: PCN-13, 27, 42, 52/60, 53, 63, 65, 66/67, 64/80, 69, 70, 71/72, 73, 74 and 75. The analytical methodology used in this study was presented in detail previously[7,13] but in brief, aliquots of the samples were fortified with ^{13}C-labelled analogues of target compounds and exhaustively extracted using mixed organic solvents. Extracts were fractionated on activated carbon, concentrated and purified using adsorption chromatography on alumina. Measurement was carried out using high resolution gas chromatography-high resolution mass spectrometry (HRGC-HRMS) at a resolution of 10,000. The method has been thoroughly validated and has been extensively used in other studies. Quality control criteria was 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.

Results and Discussion:

PCNs were detected in all analysed samples except for the cod liver oil capsules obtained in 2017 for which some congeners were below the limits of detection. The data is summarized as ΣPCN (sum of measured PCN congeners detailed in the materials and methods section) in Table 1. Excluding this sample, the concentrations for the sum of the measured PCNs (ΣPCN) in cod liver oil from the Baltic Sea ranged from 2.8 µg/kg in 1972 to 13 µg/kg in 2001. The number of samples is limited, but the gradient in this interval suggests that concentrations in the cod liver oil rose sharply over this period of almost 3 decades. The concentrations in cod liver products (canned cod liver and cod liver pate) collected from the same region in 2017 were 1.7 and 2.2 µg/kg fat. It is difficult to make the comparison between cod liver oil and the canned products (the products are reported on a lipid basis to facilitate the comparison), but the large difference may be attributable to a decline in concentrations over the 16 year period. This in turn is likely to be a result of a decline and ultimately termination, in the large scale manufacture of commercial PCN mixtures and other related chemicals which are sources of PCNs, in these regions. Additionally, emission control regulations have been in force across Europe since the last decade of the 20th century and have been accompanied by reported declining trends in similar contaminants (PCDD/Fs and PCBs) in fish[14], including in other Baltic fish species[15]. The concentrations as ΣPCN over the period of the study are plotted in Figure 1.

Region	Baltic Sea						North Atllantic - Iceland	North Atlantic - Norway	Unknown
Product	Oil	Oil	Oil	Oil	Canned liver products		L Oil	M.T. Oil	S.Oil
Year	1972	1993	2001	2001	2017[a]	2017[b]	1980	1983	2017
	Concentration in µg/kg fat								
ΣPCN	2.8	8.4	13.4	12.6	1.7	2.2	2.1	3.1	0.003

Notes: [a]"Cod livers in cod liver oil"; [b]"Pate - cod livers and vegetables"

Table 1. Summary of sample details and ΣPCN concentrations in cod liver oil and cod liver products

The cod liver oil samples that originated from the North Atlantic regions dating back to 1980 (Iceland) and 1983 (Norway) showed ΣPCN concentrations of 2.1 and 3.1 µg/kg respectively. These concentrations are comparable to the 1972 sample from the Baltic Sea at 2.8 µg/kg, but the oils were produced almost a decade later. The small number of sample points do not support a hypothesis as to whether the Baltic Sea had higher levels of contamination relative to the North Atlantic at this period, but it is instructive to note that there is advice[16] limiting the consumption of fish originating from the Baltic Sea by some countries in the region such as Finland and Sweden. Although this advice does not arise as a result of PCN contamination, it does relate to the dioxin-like (PCDD/F and PCBs) content of fish tissues. In the current context, as noted earlier, PCNs also exhibit dioxin-like behavior[1,2].

The ΣPCN concentration of 0.003 µg/kg in the commercial cod liver oil capsules obtained in Poland in 2017 is of course around 3 orders of magnitude or so lower than those of the lowest concentrations of the other oils. Cod liver oils that are produced in recent times are subjected to high levels of purification (molecular distillation, carbon filtration, etc.) to reduce the PCDD/F and PCB content of the oils[17]. Given the structural similarity, molecular size and boiling point ranges of PCNs, it is reasonable to assume that the purification processes are effective at removing PCNs as well. The concentration reported here accords well with the concentration of 0.003 µg/kg reported in 2010 for commercial cod liver obtained in the UK[7].

Work on this study will be ongoing with further dissemination on the profiles, the half-life of PCNs in Baltic cod and the contribution to dioxin-like TEQ that is associated with these PCN concentrations. It would also be instructive to estimate the human exposure to these contaminants arising from the intake of the recommended doses of cod liver oil, particularly as cod liver oil may have been given as a dietary supplement to children during the period of sampling covered by the study.

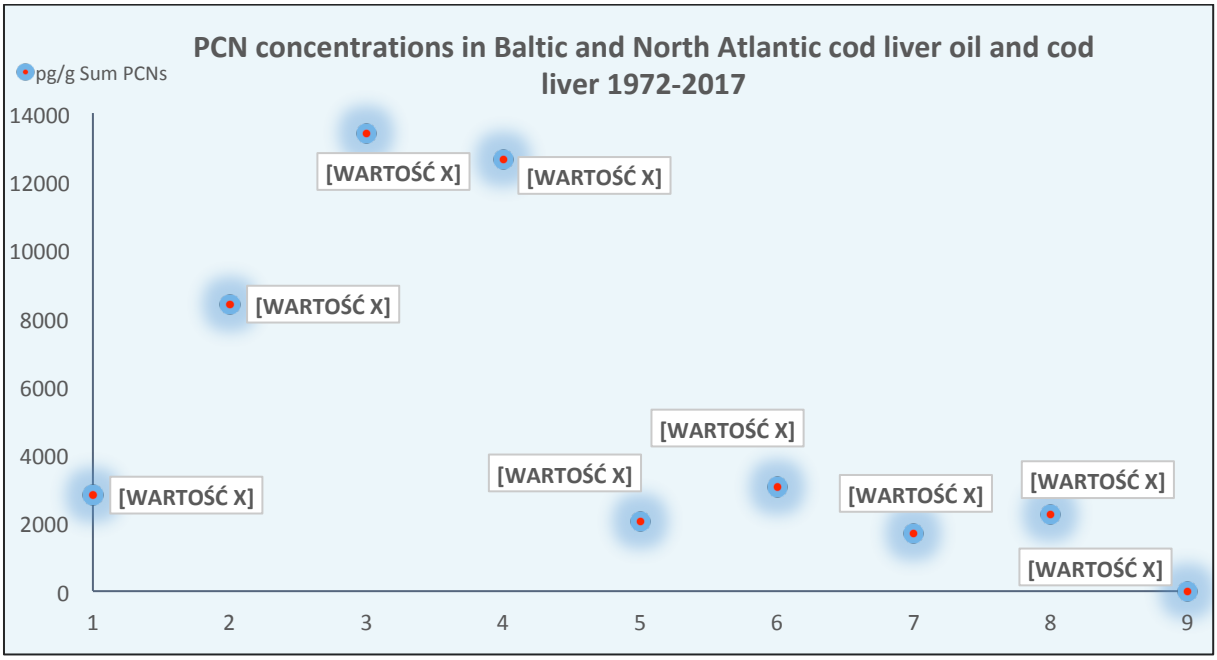

Figure 1. PCN concentrations in Baltic and North Atlantic cod liver oil and cod liver products 1972-2017

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