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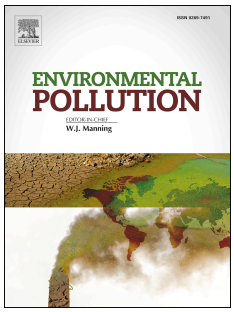

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Jerzy Falandysz, Alwyn R. Fernandes

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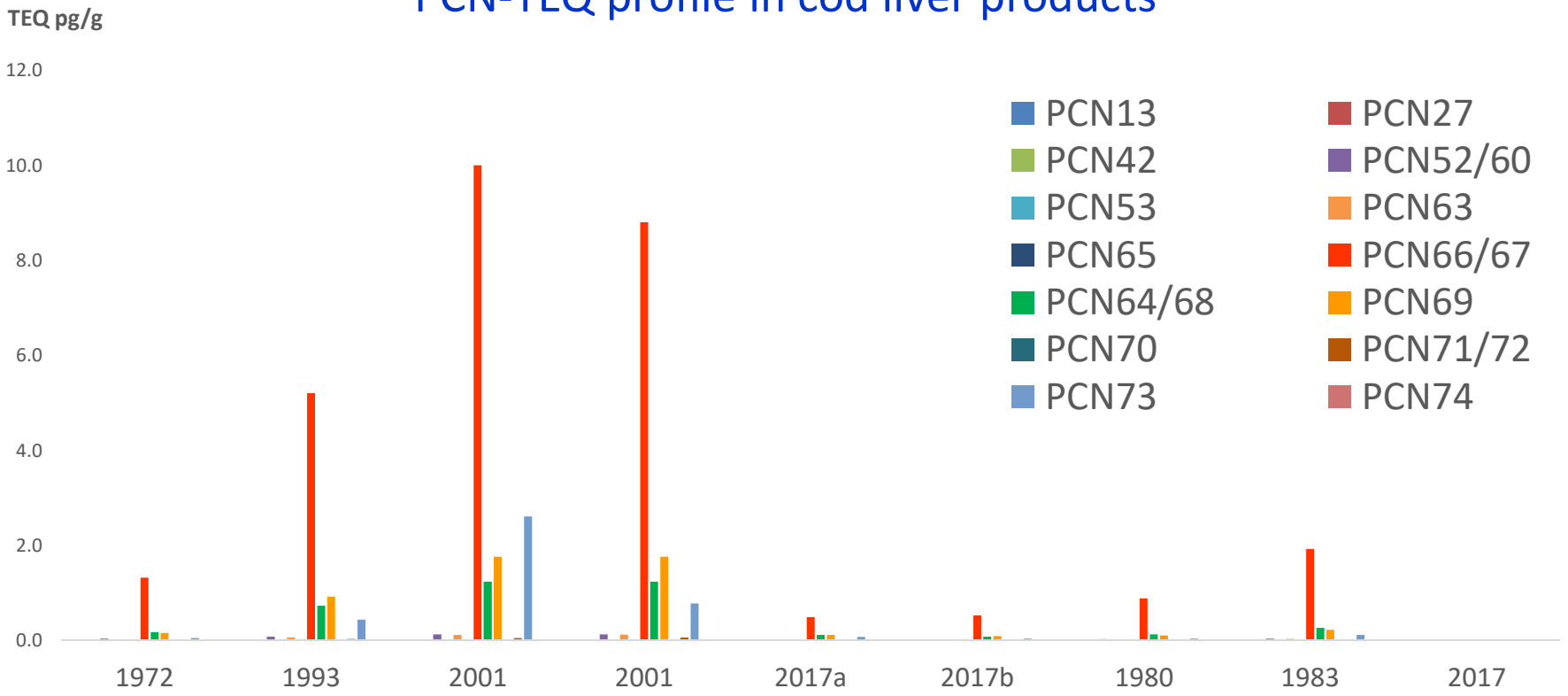
PCN-TEQ profile in cod liver products



Compositional profiles, persistency and toxicity of polychlorinated naphthalene (PCN) congeners in edible cod liver products from 1972-2017

[1,2]Jerzy Falandysz, and [3]Alwyn R. Fernandes

[1]University of Gdańsk, Environmental Chemistry and Ecotoxicology, 80-308 Gdańsk, Poland

[2]Environmental and Computational Chemistry Group, School of Pharmaceutical Sciences, Zaragocilla Campus, University of Cartagena, 130015 Cartagena, Colombia[+]

[3]School of Environmental Sciences, University of East Anglia, Norwich NR4 7TJ, UK

Capsule

The PCN contribution to dioxin-like toxic equivalence (TEQ) that was estimated for cod liver products (range 1.2 to 15.9 pg TEQ g^{-1}) was significant in comparison to the EU regulated value of 1.75 pg TEQ g-1 for dioxins in fish oils. Most of the TEQ was associated with PCNs 66/67, 64/68, 69 and 73.

Abstract

Edible cod liver products including cod liver oil and canned cod liver, sampled over the last five decades from the North Atlantic region, including the Baltic Sea were analysed for a set of persistent and toxicologically significant polychlorinated naphthalene (PCN) congeners with some of the highest relative potencies (dioxin-like toxicity) among PCNs. The targeted congeners showed a near-universality of occurrence in all samples apart from the most recent sample of cod liver oil which was assumed to be highly purified, as cod livers from the same period and location showed appreciable amounts of PCNs. The majority of dominant

congeners in legacy technical PCN mixtures were absent or occurred in low concentrations, raising the possibility that congeners arising from combustion related sources may be acquiring a greater significance following the decline and elimination of PCN production. The apparent appreciation in the relative amounts of PCN#70 in the last three to four decades may provide support for this view. The PCN contribution to dioxin-like toxic equivalence (TEQ) that was estimated for these samples (range 1.2 to 15.9 pg TEQ g^{-1}) was significant in comparison to the EU regulated value of 1.75 pg TEQ g^{-1} for dioxins in fish oils. Most of the TEQ was associated with PCNs 66/67, 64/68, 69 and 73. Although metabolic processes are likely to influence this distribution, the profile is a little different to that observed in the tissues of higher order animals where PCNs #66/67 and #73 may contribute approximately 90% to the summed TEQ.

Keywords: Dioxin-like toxicity, persistence, fish oil, marine food, toxic equivalence.

Highlights

- Highest dl-like toxicity in cod liver is associated with PCNs 66/67, 64/68, 69 and 73
- Dominant congeners that occur in PCN formulations were absent in cod-derived products
- PCN content increased in Baltic cod liver oil produced during 1972-2001
- PCNs 13 and 70 observed in cod liver products may be related to combustion sources

1. Introduction

Historically, PCNs were the second largest high volume halogenated organic chemical (after hexachlorobenzene - HCB), synthesized on an industrial scale from over a century ago and widely used and stockpiled until approximately 2000 (Yamashita et al., 2004). A number of different technical PCN mixtures of various types and applications were produced in the past in countries such as Germany, France, Italy, Japan, Poland and the United Kingdom. The combined total global production volumes of technical formulations were estimated to range from 150,000 to 400,000 tons (Falandysz, 1998; Falandysz et al., 2008; UNEP, 2017) with the Halowax series dominating in production and applications. Between them, the different Halowax formulations account for 72 of the theoretically possible 75 configurational congeners (Hanari et al., 2013).

PCNs also occur as by-products in technical polychlorinated biphenyl (PCB) formulations (Falandysz, 2007; Taniyasu et al., 2005). They are also produced unintentionally in significant quantities through thermal processes (Liu at al., 2014), at a rate that can exceed that of chlorinated dioxin (PCDD/F) formation (Takasuga et al., 2004). Combustion processes including the burning of fuels: coal, coke, wood and solid domestic waste mixture, biomass burning, forest fires, illegal burning of stockpiled hazardous/plastic waste as well as secondary non-ferrous metal smelting and iron ore sintering, etc. are considered as important current sources of PCNs in common with many other halogenated organic pollutants (Hou et al., 2017; Odabasi et al., 2016; Wyrzykowska et al., 2009; Xu et al., 2015). These processes together with emissions from other anthropogenic sources can yield the entire range of PCN congeners in significant quantities, including those that either do not occur or occur in ultra-trace or trace amounts in technical mixtures (Abad et al., 1999; Liu et al., 2014 and 2015; Odabasi et al., 2016).

The 75 PCN congeners demonstrate a full range of volatilities from highly voltile and semi-volatile, to low volatility, hydrophobic compounds. Volatility influences the gas phase

occurrence which follows the degree of chlorination with abundance ranging from Mono-CNs to OCN in descending order (Mari et al., 2008), while the reverse is observed for PCNs in the particulate phase (Harner and Bidleman, 1998). In aquatic environments, PCNs can occur in both dissolved and particle-associated forms. PCNs in suspended particulate matter can be adsorbed on soot carbon to a larger extent than bulk organic matter. Following sedimentation, PCN profiles in deep anoxic sediments can remain unchanged for decades (Ishaq et al., 2009; Persson et al., 2005).

The profiles of PCN homologues (MoCNs to OCN) buried in aquatic sediments are reported to vary depending on location and in some studies the dominant homologues were OCN > HpCNs ~ HxCNs > PeCNs > TeCNs > TrCNs (Castells et al., 2008; Zhang et al., 2015). The major PCN congeners in a background sediment in Lake Ontario were CNs #73, #66/67, #52/60, #75 and #42, in descending order of occurrence with trace concentration of 1,2,3-TrCN (#13), and 1,2,3,6,7,8-HeCN (#70) (Lega et al., 2017). Interestingly, in a study of sediment core layers from Lake Kitaura in Japan dating from the period before AD 500 to 1997/2000, a range of congeners were detected including those that are very minor constituents or are absent in the Halowax mixtures: 1,2,3-TrCN (#13), 1,3,6-TrCN (#20), 2,3,6-TrCN (#26), 1,2,3,8-TeCN (#31), 1,2,6,8-TeCN (#40), 1,3,6,7-TeCN (#44), 1,2,3,6,7-Pe (#54), 1,2,3,6,8-PeCN (#55), 1,2,3,6,7,8-HeCN (#70) (Horii et al., 2004).

Trapped within the outer waxy cuticle of pine needles, TriCNs- and TeCNs dominate the homlogue profiles from TrCNs to OctaCN, a pattern that largerly mirrors ambient air pollution with halogenated organic compounds (Orlikowska et al., 2008; Wyrzykowska et al., 2007). TriCNs and TeCNs at even higher proportions than in green plant biomass contribute to the loading of PCNs in surface layers of soils (Pan et al., 2013; Wyrzykowska et al., 2007). These findings are highly relevant because compounds such as 2,7-DiCN (#12), 1,2,3-TrCN (#13), 1,3,6-TrCN (#20), 2,3,6-TrCN (#26), 1,2,3,6-TeCN (#29), 1,2,3,8-TeCN (#31),

1,2,6,8-TeCN (#40), 1,3,6,7-TeCN (#44), 1,2,3,6,7-Pe (#54), 1,2,3,6,8-PeCN (#55) and 1,2,3,6,7,8-HeCN (#70) occur at insignificant amounts in technical PCN formulations and some, e.g. 1,3,6-TrCN (#20), 2,3,6-TrCN (#26) and 1,2,3,6,8-PeCN (#55), can be absent (Hanari et al., 2013 and 2015; Helm et al., 1999). Thus, congeners #20, #26 and #55 and to some degree also #12, #13, #29, #31, #40, #44, (#54) and #70 can be helpful in the identification of unintentionally produced PCNs, i.e. those that can be unintentionally synthesised during industrial and domestic combustion processes, uncontrolled fire accidents, bush and forest fires, incineration, etc. (Falandysz, 1998; Helm and Bidleman, 2003; Takasuga et al., 2004).

Apart from dioxin-like (dl) toxicity (Villeneuve et al., 2000), some PCN congeners also exhibit other types of toxic response (Gregoraszczuk et al., 2016). A recent study administering non-toxic doses to dams, of high purity labelled and native 1,3,5,8-TeCN (#43) showed penetration of the blood-brain-barrier and the placenta and was toxic to rat fetus (enlargement of the renal pelvis). However it was not a CYP1A1 inducer (Kilanowicz et al., 2019a). 1,2,3,5,6,7-hexachloronaphthalene (#67) which shows potent dioxin-like effects (Table 2), also causes disruption in coagulation and fibrinolysis processes and impairs the intrauterine development of rat embryos (Kilanowicz et al., 2015 and 2019b).

Edible cod liver products including cod liver oil sourced in the past from the North Atlantic region and specifically from the Baltic Sea were highly contaminated with pesticides (e.g. DDT) and PCBs (Falandysz et al., 1994). Commercial cod liver oils available from the 1990s were subjected to decontamination procedures to exclude halogenated organic pollutants resulting in lower levels of contaminants such as PCBs and PCDD/Fs (Fernandes et al. 2006), but there is very little data on these contaminants in canned cod livers (Falandysz et al., 1993). Canned cod liver products sourced from the Northern Atlantic Ocean and the Baltic Sea are currently widely available in European markets.

This study investigates congener specific occurrence (particularly those congeners that show the highest AhR potency or dl-activity and are thermodynamically more persistent) in cod liver based products along with their associated toxicity. The samples cover a relatively large timespan from 1972 to 2017 and can therefore provide indicative (due to small sample numbers) time trends. High quality literature data is also used to discuss the relative proportions of PCN congeners with respect to their origins, in order to obtain a current understanding of key food and environmental issues. The congeners may originate from legacy production of technical PCN mixtures, inadvertent formation from other sources such as technical PCB mixtures and combustion processes or environmental processes (abiotic thermodynamics and kinetics and biotic transformation/toxicokinetic), that alter the congener profiles during progression through food webs.

2. Materials and Methods

The reagents used in this study have been detailed in full, elsewhere (Fernandes et al. 2010 and 2016). Analytical standards for PCNs #13, 27, 42, 52/60, 53, 63, 65, 66/67, 64/68, 69, 70, 71/72, 73, 74 and 75 were obtained either from Wellington Laboratories Inc. Canada or Cambridge Isotope Labs, USA. ^{13}C-labelled PCN analogues of CN-42, CN-52, CN-64 and CN-75 were similarly sourced.

2.1. Cod liver products

Cod-liver oil (tran) 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:

a) Cod liver oil (Tran leczniczy, Pharmakopea Polska IV); Medicinal grade product purchased in pharmacy shops in Gdańsk, Poland (1972 – in original brown glass bottle; 100 mL),

b) Cod liver oil (1993 and 2001) obtained from a processing plant (Zakłady Rybne) in Gdynia, Poland (1993 and 2001 – in brown glass bottles, 500 mL),

c) Cod liver oil; Medicinal grade product; produced in Iceland; oleum morhuae British Pharmacopeia: (Contents 1 litre - in original can), donated by Red Cross, 1980,

d) Cod liver oil; Medicinal grade product (Medisin Tran) purchased in a pharmacy shop in Norway (Contents CA 500 ml; original green glass bottle, 1982),

e) Cod liver oil; Medicinal grade product purified and packed in gelatin capsules, 2017

f) Two types of canned cod liver products: "*Wątróbki rybne w tłuszczu własnym*" (cod liver in cod liver oil) and "*Pasztet z wątróbek dorszowych*" (pate of cod liver and vegetables) produced in the town of Łeba at the Baltic coastal region in Poland in early 2017.

Apart from the canned cod livers (which were purchased during the study) all samples were stored in refrigerated conditions at < 4^{o}C in order to maintain the integrity of the original products.

The following PCN congeners were analysed: PCNs #13, 27, 42, 52/60, 53, 63, 65, 66/67, 64/68, 69, 70, 71/72, 73, 74 and 75. The method of PCN analysis used in this study has been detailed elsewhere (Fernandes et al. 2010 and 2016). Briefly, sample aliquots of 3 – 5 g were fortified with ^{13}C-labelled surrogates of target congeners and extracted under gravity using a mixture of organic solvents and validated procedure. The extracts were fractionated on activated carbon to exclude PCBs and were then concentrated and purified using basic alumina. The instrumental determination of PCNs used high resolution gas chromatography with high resolution mass spectrometry. The full description and validation of the method used has been published earlier (Fernandes et al., 2011, 2016). The estimation of the limits of quantitation (LOQs) were made using procedural blanks as described in the recent European Commission guidelines (EC, 2017), and ranged from 0.01 to 0.1 pg/g for the different

congeners. Analytical recovery was typically in the range of 40-80% depending on the congener.

3. Results and Discussion

3.1. Contamination

All of the nineteen PCN congeners (eight co-eluted in pairs) targeted in this study, were detected in each cod liver product sampled (Table 1), apart from the oil produced in 2017 where some of the congeners were below the limits of detection. The concentrations of ΣPCN congeners in the medicinal grade and other cod liver oils were in the range 2050 to 13400 pg g^{-1} in 1972 to 2001, while in canned cod liver foods, ΣPCN ranged from 1670 to 2240 pg g^{-1} fat (730 to 1050 pg g^{-1} whole weight (ww) in 2017). In comparison to the other samples, the highly purified cod liver oil produced in 2017 showed negligible contamination with PCNs, i.e. 2.56 pg g^{-1}. Of all the studied samples, cod liver oil sourced from the Baltic Sea showed the highest levels of contamination, but the oils sourced from further west in the North Atlantic, in the regions of Iceland and Norway also showed substantial PCN concentrations (Table 1). However, reported data from other studies on contamination with PCNs in cod liver sampled from the Norwegian Sea areas and the North Sea in the 1990s and 2000-2001 showed higher concentrations than the present study with a maximum level of up to 170,000 pg g^{-1} ww in the 1990s and 210,000 pg g^{-1} ww in 2000-2001 (Frierfjord in the North Sea – as reviewed by Falandysz, 2003).

(Table 1)

3.2. Concentration profile

Apart from the 2017 cod liver oil, the highest contributors to ΣPCNs in all other samples were CNs #42 (TeCN), #52/60 (PeCN), #66/67, #69, #64/68 and #71/72 (HxCN) and #73 (HpCN) (Fig. 1). These relative contributions to ΣPCN are in good agreement with a previous report (Falandysz et al., 1996a) on whole cod from the Baltic Sea (three young specimens with body length ca. 20 cm), in which PCN #61 was additionally, a significant contributor. Other observed congeners from TeCN, PeCN and HxCN homologue groups were minor contributors (Falandysz et al. 1996a). These however were not measured in any of the samples in the present study. The 2017 cod liver oil showed a number of congeners lying below the LOQ, an alteration of the compositional profile which most likely results from the modern purification processes used to reduce the presence of environmental contaminants. Apart from this sample however, the congener profiles showed a high degree of similarity irrespective of the product or the location (Figure 1) with the dominance of CNs #42, #52/60 and #66/67. As the literature shows, (Falandysz et al., 1996; Falandysz and Rappe, 1996; Fernandes et al., 2010; 2011; 2018; 2019 Kannan et al., 2001) this profile is not restricted to cod and is also common to other marine fish species such as sardines, mackerel, herring, etc., from other North Atlantic, the Mediterranean Sea or the Great Lakes (Northern America) waters which show a similar dominance of congeners #52/60 and #66/67 (CN#42) was not measured in some of these studies). Fresh water species show some differences which may arise from a greater susceptibility to terrestrial inputs (e.g. leaching of PCN/PCB formulations from products/materials containing them) or through species selective metabolism. In these freshwater species, CNs #71/72 also appears as a dominant congener in addition to CNs #52/60 (Rose et al., 2015).

(Figure 1)

3.3. Persistency

With the exception of 1,2,3,5,7,8-HxCN (#69), congeners that are dominant in technical PCN formulations do not appear to occur in marine food chains and similarly, occurred as minor components or were not detected in the cod liver products examined in this study (Table 1). Technical PCN formulations show a strong dominance by individual congeners such as: 1-MoCN (#1) of MoCNs; 1,2-/1,6-DiCNs (#5/7) of DiCNs; 1,2,7-/1,4,6-TrCNs (#21/24); 1,2,4-TrCN (#14), 1,4,5-TrCN (#23) and 1,2,7-TrCN (#17) of TrCNs; 1,2,5,8-TeCN (#38), 1,4,5,8-TeCN (#46), 1,2,4,6-TeCN (#33), 1,2,4,8-TeCN (#35) and 1,4,6,7-TeCN (#47) of TeCNs; 1,2,4,5,8-PeCN (#59), 1,2,4,7,8-PeCN (#62), 1,2,3,5,8-PeCN (#53), 1,2,4,5,6-PeCN (#57) and 1,2,4,6,8-pentaCN (#61) of PeCNs; 1,2,4,5,6,8-/1,2,4,5,7,8-HxCN (#71/72), 1,2,3,5,7,8-HxCN (#69), 1,2,3,4,5,8-HxCN (#65), 1,2,3,4,5,7-/ 1,2,3,5,6,8-HxCN (#64/68) and 1,2,3,4,5,6-HxCN (#63) of HxCNs, 1,2,3,4,5,6,8-HpCN (#74) of HpCNs and 1,2,3,4,5,6,7,8-OCN (#75) (Falandysz et al., 2000 and 2008, Hanari et al., 2013; Helm et al., 1999).

Apart from photo-degradation in the atmosphere and upper hydrosphere, it is evident that PCNs also undergo metabolic degradation in aquatic food chains starting, e.g. from plankton and mussels that show low capacity for metabolising halogenated POPs (Fernandes et al., 2008) > to fish species that feed on planktonic and benthic organisms up to highly predatory fish species like cod that are among the top piscivorous predators > to higher order animals such as the great black cormorant (*Phalacrocorax carbo*), thick-billed murre (*Uria lomvia*) > marine mammals > top avian predators (peregrine falcon *Falco peregrinus*, white-tailed eagle *Haliaeetus albicilla*) (Braune and Muir, 2017; Cui et al., 2018; Falandysz and

Rappe, 1996; Falandysz et al., 1996a, 1996b, 1997, 1998; Gewurtz et al., 2018; Koistinen et al., 2008; Lundgren et al., 2002; Vorkamp et al., 2019).

Some PCN congeners are not present in technical mixtures such as Halowax but are formed in combustion/thermal related emissions such as 1,3,6-TrCN (#20), 2,3,6-TrCN (#26) and 1,2,3,6,8-PeCN (#55). As mentioned earlier, these have been recorded in sediment cores in Japan: PCN#20 (6.6 to 0.065 pg g^{-1} dry matter, dm) and PCN#26 (1.4 to 0.062 pg g^{-1} dm), and PCN#55 in one layer (0.55 pg g^{-1} dm; years 1984-85) (Horii et al., 2004), but there is currently no known data available to the authors on the occurrence of these congeners in environmental biota.

3.4. PCN #70 time trends and compositional relevance

There are estimates for the volume of PCNs manufactured during particular periods, but there is no global inventory for production and certainly no quantitative estimates for individual congeners occurring in technical PCN formulations. It is estimated that inadvertent PCN formation arising from the manufacture of PCBs is around 0.0067% of the quantity of PCBs produced (Falandysz, 1998, 2007; Taniyasu et al., 2005), which in terms of global production was estimated at 169 tons of PCNs (Yamashita et al., 2000). The compositional profile of these inadvertently formed PCNs is thought to be the same as those from intended PCN production, because the production processes for both, PCBs and PCNs, follows a roughly similar scheme of synthesis and catalysis during the chlorination of the parent substrate (biphenyl or naphthalene).

The situation regarding PCN formation from combustion and other thermal processes is similar. There is no known inventory for ΣPCNs or individual congeners produced from processes such as intentional combustion of fuels and wood for heating, waste incineration

and metallurgy, while the volume of PCNs formed during bush and forest fires, open burning of landfilled wastes and fire accidents have not really been considered. As mentioned earlier, apart from 1,2,3,5,7,8-HxCN (#69), all other major contributors to ΣPCNs in cod liver products (Fig. 1) were minor constituents in technical PCN formulations. As PCNs have not been manufactured for several decades now, this observation raises the important question of whether combustion related sources are becoming more important than evaporative emissions from legacy sources and perhaps more importantly whether this pathway leads to the production of congeners that are relatively more persistent and more toxic?

During analytical measurement, a number of chloronaphthalene congeners co-elute in pairs or triplets depending on the chromatographic conditions and there have been some attempts to resolve these co-elutions using high resolution GC with various liquid phases, e.g. Rt-βDEXcst columns (Helm et al., 1999; Lega et al., 2017), and also by employing two-dimensional GC methods (Hanari et al., 2013 and 2015). Practically however, most of the data generated on PCN occurrence in biological or environmental matrices to date involves more conventional methodology providing data that is either on homologue contents, or more recently targeted towards the more toxic individual congeners which still leaves some pairs unresolved as in the present study. There is no doubt that a key requirement for verifying the presence of a specific PCN congener (especially of minor congeners and those that are more prone to degradation) is complete separation of all 75 congeners. This outcome would be immensely helpful to explain the susceptibility of congeners to abiotic degradation and biotransformation with the aim of predicting their environmental fate and possible toxic impacts based on occurrence, thermodynamic and biological data.

Among the PCN congeners that were detected in cod liver products in this study, the occurrence of two minor constituents, 1,2,3-TrCN (#13) and 1,2,3,6,7,8-HeCN (#70) may be related to combustion sources. PCN#13 and PCN#70 were found to occur in sediment cores

(dating from before 500 A.D. to 2000) from Lake Kitaura in Japan (Horii et al., 2004). It has been hypothesized that TrCNs (thus also MoCNs and DiCNs) are more prone to infiltration down to greater depths in sediment layers which could explain their occurrence and prevalence in some of the deepest Lake Kitaura sediment layers dating back to earlier than 500 A.D. However, a later study by Ishaq et al. (2009), reported that the profile of PCNs remained unchanged within different layers of a sediment core in deep anoxic waters (those with dissolved oxygen concentration of less than 0.5 milligrams per litre). It is difficult to decipher the original PCN profiles from earlier eras because there is practically no information on the thermodynamics and formation chemistry of individual PCNs that are formed during bush and forest fires which were probably the ancient sources of those compounds, particularly those of lower molecular mass. Jansson et al. (2009) concluded that in some thermal processes, "PCNs formation is likely to occur via more than one pathway, including chlorination of naphthalene that is already present, *de novo* synthesis from PAHs and, possibly, chlorophenol condensation".

PCN#70 is considered to have poor water solubility, poorer than lower chlorinated congeners including PCN#13 (TrCN) but there is no original data on #70 solubility (Jakobsson et al., 2000). It also has a much higher $K_{O/W}$ value and general persistency than #13 or any of the other TrCNs and PeCNs (Falandysz et al., 2001). Thus, despite the small number of data points over the 40-50 year time span of the samples in the present study (Table 1), PCN#70 is more suitable for time-trend analyses. The data for PCN#70 from this study and from the Lake Kitaura sediment core records were thus compiled chronologically in Fig. 2 and appear to show a gradual of PCN#70 appreciation in more recent years which may result from relatively higher persistence, increasing levels of occurrence (e.g. from combustion related sources) or a combination of the two.

(Figure 2)

3.5. ΣPCN time trend (literature relevance)

The very small volume of literature data on PCN does not support studies on time trends in biological and abiotic materials. Similarly, the small amount of archived samples in this study can only provide at best, an indicative vector of the concentrations in marine products. However, ΣPCN in species from different Baltic Sea trophic webs such as cod, herring (*Clupea harengus*) and guillemot (*Uria aalge*) eggs, appear to be decreasing. Levels in herring from 1982 to 2009 showed a decline but levels between 1985 to 2008 were rather variable and without any apparent decrease, and guillemot's eggs showed a decline from 1974 to 2004, but were relatively low and stable between 2004 and 2009 (Haglund et al., 2010). The PeCNs and HxCNs levels determined in the livers of arctic cod (*Arctogadus glacialis*) caught in the European Arctic in the region of Vestertana Fjord in Norway between 1987 and 1998 were stable (Sinkkonen and Paasivirta, 2000). There was a significant decrease of lipid-normalized concentrations of PCN#53, #54 and #63 in the eggs (n = 41) of peregrine falcon collected in South Iceland between 1986-2017, but the concentrations were still considered to be high (Vorkamp et al., 2019). A decline in ΣPCNs between 1975 and 2014 was noted in guillemot (*Uria lomvia*) eggs from Prince Leopold Island, Nunavut in the Canadian Arctic (Braune and Muir, 2017) and similarly, ΣPCNs declined by 98% between 1984 and 2003, in the blubber of pups of non-migratory harbor seals (*Phoca vitulina*) from the Strait of Georgia, Juan de Fuca Strait and Puget Sound in the Salish Sea (Ross et al., 2013).

Data on abiotic media showed PCNs decreasing in sediment cores from the UK with peaks in 1980 and in 1960s (Gevao et al., 2000). A similar study on two sediment cores from the Jiaozhou Bay (Yellow Sea) showed that PCN contamination within the Bay decreasing

from the elevated levels in the early 1990s, to 34.9 pg g^{-1} dm around 2000, while outside the Bay the peak levels of the mid-1970s decreased in later years up to the late 1990s (Pan et al., 2012). Chloronaphthalenes in archived soils (1944-1986) from Broadbalk and Luddington in the U.K. showed a peak in 1956 with significant ($p < 0.05$) increasing trends for some CNs that were considered to be associated with combustion such as CN#29, #51, #52/60, #54, and #66/67 which could suggest "that combustion related sources are more important now than they were in the past" (Meijer et al., 2001). However, it should be pointed out, that photodegradation of higher molecular mass congeners contained in the technical PCN formulations of the Halowax series (Halowax 1014 and Halowax 1051) leads to temporal increases in the production of compounds such as CNs #52/60, #66/67 (Hanari et al., 2019).

3.6. Compositional toxicity of dioxin-like congeners

Data on total and congener-specific dioxin-like toxic equivalence (TEQ) of PCNs contained in cod liver products are presented in Table 2. The REP (relative potency) values that were applied for the TEQ calculations (Table 2) have been used and described in a number of earlier studies (Fernandes et al., 2010; 2011; 2017; 2018; Falandysz et al., 2019) and are based on a meta-analysis of potency data from existing studies (Falandysz et al., 2014; Fernandes et al., 2010, 2017).

TEQ is considered to be a cumulative response for different classes of dioxin-like compounds, which include regulated (dl-PCBs and PCDD/Fs) as well as others (e.g. PCNs, PBDD/Fs) that are not yet regulated (Fernandes et al., 2014; Van den Berg et al., 2013). The TEQ estimated for these individual congeners was combined to provide a summed TEQ which ranged from 1.2 to 15.9 pg g^{-1} in natural cod liver oils produced in 1972 - 2001 and 0.003 pg g^{-1} in decontaminated (purified) cod liver oil produced in 2017. Nonetheless, the

PCN TEQ contribution arising from these samples is significant, particularly when compared to the currently regulated limit of 1.75 pg g^{-1} for PCDD/F TEQ in fish oil (EC, 2011).

TEQ compositional profiles for PCNs (Fig. 3) were roughly similar for natural cod liver oils and canned cod livers with dominant (%) contributors being: #66/67 (63 to 75 %), #69 (8 to 14 %), #73 (3 to 16 %) and #64/68 (8 to 12 %). The relative contribution of these congeners to summed TEQ is a little different to the average distribution observed in the tissues of higher order domesticated animals (cows, sheep, pigs etc.), where the TEQ from PCNs #66/67 and #73 make up around 90% of the summed TEQ (Fernandes et al., 2010). The profile for the purified cod liver oil which contained very low PCN concentrations was different: #66/67 (34 %), #69 (11%), #73 (8), and #64/68 (15%), most likely due to the selective removal during purification as well as the uncertainty during measurement at these low concentrations.

Table 2

(Figure 3)

Conclusions

The PCN congeners selected for study in this investigation occurred near universally in all samples apart from the most recent purified cod liver oil. However canned cod liver obtained during the same year from the same area (Baltic Sea) showed substantial occurrence of all PCN congeners. The more recent literature on marine sediment sequestration of PCN congeners shows that anoxic waters are stable sinks for historic depositions of combustion associated particulate bound PCN congeners. The relevance of these findings coupled with the congener profiles of the cod liver products investigated which showed that the majority of dominant congeners in technical PCN mixtures were absent in the cod liver oils, poses the

question of whether combustion related sources of PCNs becoming more significant than the legacy production of technical mixtures. The apparent appreciation in the relative amounts of PCN#70 in the last three to four decades may provide support for this view.

The examination of toxic equivalence in the cod liver products shows a significant proportion of dioxin-like toxicity, most of which is associated with PCNs 66/67, 64/68, 69 and 73. Although metabolic processes are likely to influence this distribution, the relative contribution of these congeners to summed TEQ is a little different to that observed in the tissues of higher order animals where the TEQ from PCNs #66/67 and #73 make up around 90% of the summed TEQ.

Disclaimer

The authors assert no conflict of interest.

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683 Figure legends

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685 Figure 1. Distribution of PCN congeners in cod liver products (in clour available on-line
686 only).

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688 Figure 2. Chronology of PCN #70 concentrations in dated sediment cores and cod liver
689 products Blue: Sediment, pg g^{-1} dry matter.Green: Cod liver products pg g^{-1} fat.(in clour
690 available on-line only).

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692 Figure 3. Congener specific TEQ profile for cod liver oils and products: 2017a – canned cod
693 liver; 2017b – canned cod liver & vegetable pate (in clour available on-line only).
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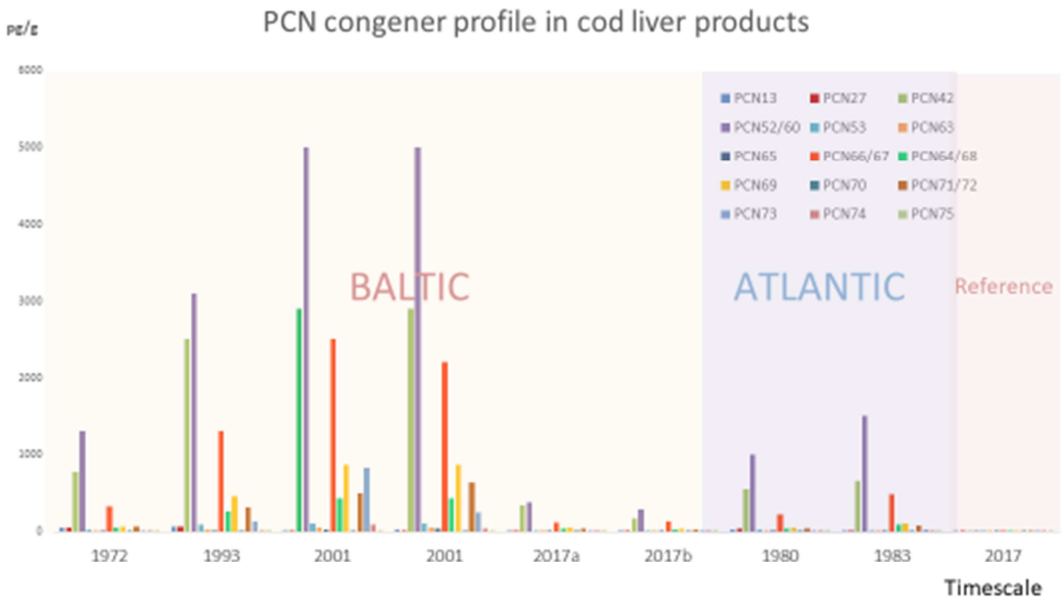

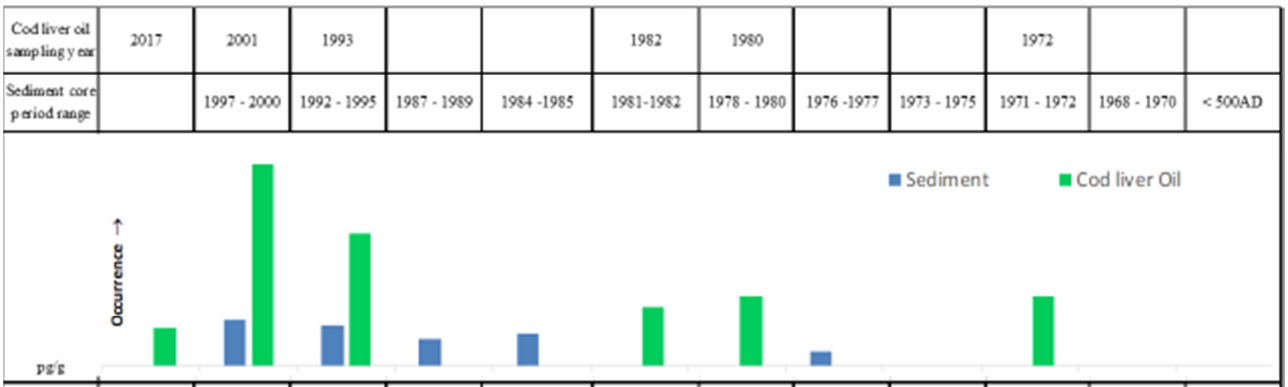

Cod liver oil sampling year	2017	2001	1993			1982	1980			1972		
Sediment core period range		1997 - 2000	1992 - 1995	1987 - 1989	1984 -1985	1981-1982	1978 - 1980	1976 -1977	1973 - 1975	1971 - 1972	1968 - 1970	< 500AD
Sediment	No data	0.84	0.76	0.5	0.61	0	0	0.28	0	0	0	0
Cod liver Oil	0.7	3.8	2.5	No data		1.1	1.3	No data		1.3	No data	

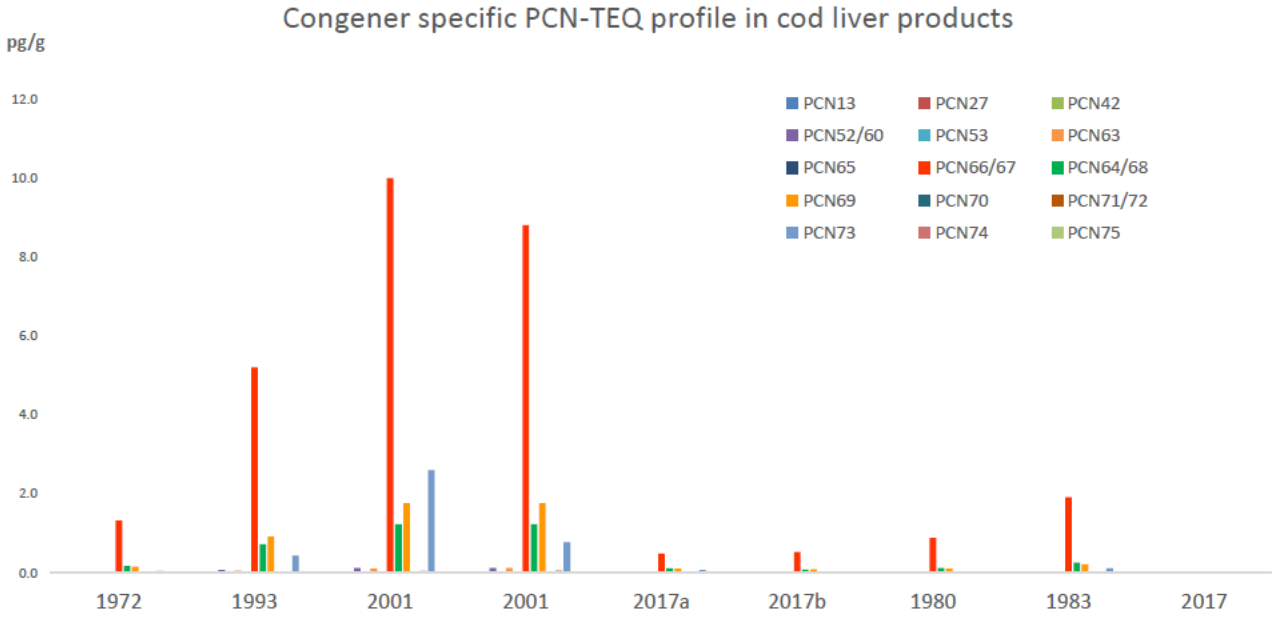

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Table 1. PCNs (pg g^{-1} fat) in cod liver oil and canned liver products (pg g^{-1} fat // pg g^{-1} whole weight) sourced from regions of the North Atlantic in 1972 – 2017

	Region of the North Atlantic								
	Baltic Sea						Iceland	Norway	Unknown
	Cod liver oil	Cod liver oil	Cod liver oil	Cod liver oil	Canned liver products		Cod liver oil	Cod liver oil	Cod-liver oil
PCN no.	1972	1993	2001	2001	2017	2017	1980	1982	2017
13	54	67	19	36	7.7 // 4.9	12.2 // 3.9	37	20	0.33
27	63	76	11	16	9.5 // 6.0	0.8 // 0.3	38	3.6	0.35
42	790	2500	2900	2900	544 // 340	522 // 170	550	670	0.42
52/60	1300	3100	5000	5000	613 // 380	884 // 290	1000	1500	0.37
53	32	99	110	110	31 // 19	19 // 6	37	20	0.09
63	9	29	55	59	11 // 7.0	8.9 // 2.9	7.2	15	0.12
65	6.9	23	34	49	6.0 // 3.8	5.8 // 1.9	4.8	7.1	0.08
66/67	330	1300	2500	2200	196 // 120	407 // 130	220	480	0.29
64/68	61	260	440	440	64 // 40	87 // 28	45	93	0.09
69	76	460	880	880	88 // 55	141 // 46	51	110	0.08
70	1.3	2.5	3.6	4	0.7 // 0.5	0.7 // 0.2	1.3	1.1	0.08
71/72	68	320	500	640	67 // 42	111 // 36	43	82	0.06
73	16	140	840	250	38 // 24	36 // 12	12	37	0.09
74	3.7	19	100	45	7.7 // 4.8	6.7 // 2.2	2.8	10	0.02
75	0.88	8.2	15	14	2.2 // 1.4	1.4 // 0.45	0.74	1.7	0.07
Sum, rounded	2810	8400	13400	12600	1670 // 1050	2240 // 730	2050	3050	2.56

Notes: A and B = two types of canned cod-liver products: "cod livers in own juice" (fat at 62.8%)[A] and "pate, cod liver & vegetables" (fat at 32.3%)[B] produced in the town of Łeba (Poland) in 2017.

Table 2. Toxic equivalents (TEQ) of PCNs in cod-liver oil and canned liver products (pg g^{-1} fat and pg g^{-1} whole weight[B,C])

		Region of the North Atlantic							
		Baltic Sea					Iceland	Norway	Unknown
	REP values	Cod liver oil	Cod liver oil	Cod liver oil[A]	Canned liver products		Cod liver oil	Cod liver oil	Cod liver oil
PCN no.		1972	1993	2001	2017[B]	2017[C]	1980	1982	2017
13	0.0000032	0.0002	0.0002	0.0001	< 0.000	< 0.000	0.0001	0.0001	< 0.000
27	0.00000195	0.00012	0.00015	0.0002	0.00001	< 0.000	0.00007	0.00001	< 0.000
42	0.0000047	0.0037	0.0118	0.0136	0.0016	0.0008	0.0026	0.0031	< 0.000
52/60	0.000025	0.0325	0.0775	0.125	0.0096	0.0071	0.0250	0.0375	< 0.000
53	0.0000018	0.0001	0.0002	0.0002	0.00004	0.00001	0.00007	0.00004	< 0.000
63	0.002	0.018	0.0580	0.114	0.01380	0.00575	0.01440	0.030	0.0002
65		< 0.000	< 0.000	< 0.000	< 0.000	0.000	< 0.000	< 0.000	< 0.000
66/67	0.004	1.320	5.200	9.400	0.491	0.526	0.8800	1.920	0.0012
64/68	0.0028	0.171	0.728	1.230	0.1130	0.0786	0.1260	0.260	0.0005
69	0.002	0.152	0.920	1.760	0.1100	0.0914	0.1020	0.220	0.0004
70	0.005	0.0065	0.0125	0.019	0.0023	0.0012	0.0065	0.011	0.0009
71/72	0.00009	0.0061	0.0288	0.0513	0.0038	0.0032	0.0039	0.0074	< 0.000
73	0.0031	0.0496	0.434	1.670	0.0733	0.0365	0.0372	0.115	0.0003
74	0.0000041	< 0.000	0.0001	0.0003	< 0.000	< 0.000	< 0.0000	< 0.000	< 0.000
75	0.00001	< 0.000	0.00008	0.0002	< 0.000	< 0.000	< 0.0000	< 0.000	< 0.000
TEQ		1.76	7.47	14.40	0.82	0.75	1.20	2.57	0.003
*Proportion of regulated TEQ		1.01	4.27	8.23	0.47	0.43	0.69	1.47	0.002

Notes: A (mean for year 2001, Table 1; max. 15.9 pgTEQ g^{-1} fat); B and C = two types of canned cod-liver products: "cod livers in own juice"[B] and "pate, cod liver & vegetables"[C] produced in the town of Łeba (Poland) in 2017, *PCN TEQ as a proportion of the regulated PCDD/F TEQ (see Ref. EC, 2011)

AUTHOR STATEMENT

Manuscript title:

Compositional profiles, persistency and toxicity of polychlorinated naphthalene (PCN) congeners in edible cod liver products from 1972-2017

All persons who meet authorship criteria are listed as authors, and all authors certify that they have participated sufficiently in the work to take public responsibility for the content, including participation in the concept, design, analysis, writing, or revision of the manuscript.

Category 1
Conception and design of study: **J. Falandysz/A. Fernandes**;

acquisition of data: **A. Fernandes/J. Falandysz;**

analysis and/or interpretation of data: **J. Falandysz/A. Fernandes**;

Category 2

Drafting the manuscript: **J. Falandysz/A. Fernandes**;

revising the manuscript critically for important intellectual content **A. Fernandes/J. Falandysz**.

Category 3
Approval of the version of the manuscript to be published (the names of all authors must be listed):

J. Falandysz/A. Fernandes;

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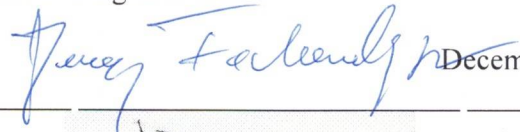
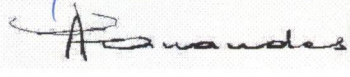
Jerzy Falandysz		December 17, 2019
Alwyn Fernandes		December 17, 2019

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