INVESTIGATION INTO THE OCCURRENCE OF POLYCHLORINATED NAPHTHALENES IN UK RETAIL FOODS

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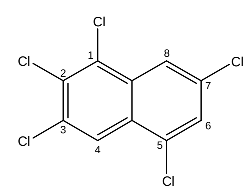
Abstract

Polychlorinated naphthalenes (PCNs) were manufactured and used in the middle part of the last century. They are a group of persistent organic pollutants, some of which are reported to have dioxin-like toxicity. A series of the more highly substituted congeners (penta- to octa-) have been measured in a range of UK retail foods. PCNs were detected in all of the samples tested. Fish contained the highest PCN levels (concentration of total PCNs ranging from 0.73-37.3 ng/kg whole weight), as well as the biggest range of congeners, with PCN 52/60 (1,2,3,5,7-pentaCN/1,2,4,6,7-pentaCN) being the most abundant. Eggs and poultry contained a similarly wide range of congeners, but at lower levels (0.48-8.29 ng/kg whole weight). Occurrence was lowest in meat and dairy products (0.19-6.09 ng/kg whole weight). Further studies will be required for a fuller understanding of UK dietary exposure to PCNs, but there are no indications of an immediate risk to health.

Introduction

Polychlorinated naphthalenes (PCNs) are part of a much wider group of chlorinated polycyclic aromatic hydrocarbons. They were used during a large part of the last century as an industrial chemical in product formulations such as Halowax. They can also be formed in small amounts by *de Novo* synthesis during combustion processes[1]. Like polychlorinated biphenyls (PCBs), PCNs are hydrophobic, thermally stable, resistant to oxidation, of low flammability and good electrical insulators. They were therefore widely used in electrical equipment. However, the similarity of the structure and stability of PCNs to dioxins and certain PCBs also gives them dioxin-like toxicological properties. Chloracne and liver disease have been reported from occupational exposure to PCNs and exposed workers are also reported to have a slightly raised overall cancer risk. The manufacture of PCNs is now banned and their use greatly restricted. Due to their dioxin-like toxicity, Toxic Equivalency Factors (TEFs) have been proposed for some PCN congeners.[9-13]

PCN-52



Until recent years, the lack of suitable analytical methodology and scarcity of reference standards for individual PCN congeners have hampered work to investigate their occurrence in the environment, biota and food. Early work to determine the levels of PCNs in fish was generally associated with environmental monitoring and confirmed their ability to bioaccumulate[2-4]. There are a small number of reports of levels in fish with a view to assessing human exposure[5-6]. PCNs have been reported in domestic animals[7] and in human milk[8]. The European Food Safety Authority (EFSA) concluded in 2004 that compounds exhibiting dioxin-like toxicity should be considered for Toxic Equivalency Factors but that prioritisation should be based on exposure[14]. Information on dietary exposure of humans to PCNs is currently lacking. Two surveys of foods have been conducted in Spain, indicating that the highest PCN concentrations were to be found in fats and oils, cereals, fish, dairy products and meat [5,15]. The UK Food Standards Agency began investigating the occurrence of PCNs in retail foods in 2007. Initial results were presented at the Dioxin 2008 symposium [16].

Methods and materials

Samples were purchased in 2007. These included individual samples of meat and offal (n=9), eggs and poultry (n=9), fish and fishery products (n=13) and milk and dairy products (n=9), together with one cod liver oil sample and composite samples of vegetables, fruit and bread. The samples were not intended to cover the entire food range or UK diet in a comprehensive manner but rather to establish whether PCNs can be detected in the various food matrices and at what levels. The choice of samples was directed generally towards the types of foods in which environmentally persistent lipophilic compounds would be most likely to accumulate, i.e. fish and animal-derived products with a high fat content.

Samples were analysed by the Food and Environment Research Agency (formerly Central Science Laboratory). Dry solids, powders and oils were homogenised prior to extraction by roller-mixing, milling or blending. 'Wet' samples and liquids were homogenised by blending and freeze-dried prior to extraction. In the case of fishery products, only the parts normally consumed were analysed.

Table 1. Congeners measured

PCN 52	1,2,3,5,7-pentaCN
PCN 53	1,2,3,5,8-pentaCN
PCN 66/67	1,2,3,4,6,7-hexaCN/1,2,3,5,6,7-hexaCN
PCN 68	1,2,3,5,6,8-hexaCN
PCN 69	1,2,3,5,7,8-hexaCN
PCN 71/72	1,2,4,5,6,8-hexaCN/1,2,4,5,7,8-HexaCN
PCN 73	1,2,3,4,5,6,7-heptaCN
PCN 74	1,2,3,4,5,6,8-heptaCN
PCN 75	Octachloronaphthalene

Table 1 contains a list of the PCN congeners included in the analysis. This includes some that have been reported to have dioxin-like toxicity, although the selection was limited by the availability of suitable internal standards. Tetrachloronaphthalene, which has been reported in other studies, was not included as it is considered to be of little dioxin-like toxicological significance. $^{13}C_{10}$ labelled PCNs 42, 52, 64 and 75 were used as internal standards.

Although the physico-chemical nature of PCNs suggests that they could be extracted and purified following a similar method to dioxins and PCBs, beginning with accelerated solvent or soxhlet extraction, direct elution through activated carbon allows fractional separation of the PCNs from non-planar compounds including PCBs, which can interfere during the quantification stage.

An aliquot of the prepared, homogenized sample (sufficient to provide 2-5 g of lipid) was fortified with a known amount of $^{13}C_{10}$-labeled PCN internal standard mix (ca. 50 µL). For extraction and purification, the samples were equilibrated and blended with hexane and acid modified silica gel and passed through a multi-layer column containing anhydrous sodium sulphate (30g), acid modified silica gel (50g), sodium sulphate (10g) and silanised glass wool, and eluted through a second column with activated carbon dispersed on glass fibre. The carbon column was disconnected and reverse-eluted with 100 ml of toluene to obtain the fraction containing the PCNs.

Individual PCN congeners were analysed using high resolution gas chromatography – high resolution mass spectrometry (HRGC-HRMS). These measurements were performed on a Micromass Autospec Ultima instrument connected to a Hewlett Packard 6890N gas chromatograph and a CTC Analytics PAL GC autosampler. The gas chromatograph was fitted with a 60m x 0.25mm J&W DB-5 MS fused silica capillary column. Quantification was carried out on the basis of stable isotope dilution of the ^{13}C labelled surrogates (PCNs 42, 52, 64 and 75) and internal standardisation. The laboratory has taken part in a number of inter-laboratory trials for dioxins and non-*ortho* polychlorinated biphenyls for which the analytical methodology is very similar[15], including several rounds of "Dioxins in food". All results were assessed against published analytical quality assurance criteria[17].

Table 2. Summary of results by food group

Sum PCN (ng/kg whole weight)	**Meat / Offal**	**Eggs / Poultry**	**Fishery products**	**Milk / Dairy**
Minimum	0.19	0.48	0.73	0.19
Median	0.53	1.47	18.9	0.82
Mean	**1.64**	**2.38**	**19.9**	**1.51**
Maximum	5.69	8.29	37.3	6.09

Results and discussion

A summary of results is presented in Table 2, which shows the *Lower Bound* sums of congeners detected. The highest levels of PCNs were found in fish samples, which is not unexpected since fish are normally most exposed to environmental contaminants. In the other groups, the ranges of contamination were broadly similar to each other, although it must be noted that this is based on a relatively small number of samples.

Detailed results (on a whole weight basis) for individual congeners in each sample are presented in Tables 3a-d. At least one PCN congener was detected in all of the samples analysed. In fish, PCN 52/60 was much the most abundant, accounting for 70 to 90% of the total. PCN 52/60 was also found in most of the samples in the eggs and poultry and dairy samples, although it was less abundant (30-60% in eggs and poultry and 0-30% in milk and dairy products). In meat and offal, PCN 52/60 was found in only one sample each of beef and lamb. PCN 52/60 has not, however, been reported to show dioxin-like activity. Of the congeners reported to demonstrate dioxin-like activity, PCNs 66/67 were the most prevalent, followed by PCN 73. Other than in some of the fish samples, the highest levels of PCN 66/67 were found in one sample each of lamb shoulder and lamb liver and these also contained the highest levels of PCN 73 detected in any samples including fish.

Table 4. Proposed TEFs

PCN 52	**1,2,3,5,7-pentaCN**	0.000025
PCN 53	1,2,3,5,8-pentaCN	0.0000018
PCN 66 (or 66/67)	1,2,3,4,6,7-HexaCN	0.004
PCN 67	1,2,3,5,6,7-HexaCN	0.001
PCN 68	1,2,3,5,6,8-HexaCN	0.0028
PCN 69	1,2,3,5,7,8-HexaCN	0.002
PCN71 (or 71/72)	1,2,4,5,6,8-HexaCN	0.000009
PCN 73	1,2,3,4,5,6,7-HeptaCN	0.0031
PCN 74	1,2,3,4,5,6,8-heptaCN	0.0000041
PCN 75	Octachloronaphthalene	0.0001

As noted earlier, TEFs have been proposed for PCNs in the literature[9-13]. These tend to apply to the more highly-substituted PCN congeners containing at least six chlorine atoms. Table 4 lists some of the proposed TEF values and the TEQs derived from these for some of the more contaminated samples are shown in Table 5. These are only intended to provide some context by giving an indication of how the levels might compare with levels of dioxins and dioxin-like PCBs. All of the results are expressed on a whole weight basis. In fish, typical dioxin plus dioxin-like PCB WHO-TEQ levels are 3-4 ng/kg for sprats and herring, 2-3 for farmed salmon and 1-2 for eel and trout, i.e. about two orders of magnitude higher. In the case of lamb carcass meat, the dioxin/PCB TEQ content is normally expressed on a fat basis and would typically be 1-2 ng/kg. The higher of the results for lamb shoulder in Table 5 would be equivalent to a fat based level of 0.13 ng/kg, i.e. about one order of magnitude below the dioxin/PCB TEQ level, suggesting that PCNs could potentially make a meaningful contribution to the overall TEQ. In the case of lamb liver, the whole weight dioxin/PCB TEQ levels vary considerably, from <0.1 to about 2.0 ng/kg. It is therefore more difficult to put the results for lamb liver into context. Future investigations would need to involve measuring a wider range of POPs in the same samples.

Table 5. Derived TEQs for selected samples

	No. of samples	PCN TEQ ng TEQ/kg
Eel	2	0.02, 0.02
Sprats	2	0.02, 0.02
Salmon (farmed)	2	0.02, 0.02
Herring	2	0.006, 0.01
Rainbow trout	2	0.005, 0.008
Lamb shoulder	2	0.003, 0.02
Lamb liver	2	0.001, 0.02
Butter	1	0.02

This investigation covered only a small number of samples from a limited range of food groups. The main objective was to develop suitable methodology and establish whether it was possible to detect polychlorinated naphthalenes in UK foods. This has been successfully achieved. However, it is not possible at this stage to make a meaningful assessment of health implications. There are insufficient data to reliably estimate dietary exposures. Furthermore, there is insufficient toxicological information to fully understand the relevance to human health. For instance, not only have the proposed TEFs yet to be endorsed by toxicological committees but there may be other adverse health effects that would not be adequately covered in the TEF system. Furthermore, analytical standards of suitable purity are not yet available for all of the congeners of potential concern. Nevertheless, UK toxicologists are satisfied that the results do not indicate an immediate human health concern. Future investigations will focus on producing a reliable estimate of human exposure to PCNs and understanding their occurrence in the food chain.

Acknowledgements

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Table 3a. Levels found in meat and offal (ng/kg whole weight)

	Pork sausages	Braising steak	Rump steak	Ox liver	Lamb shoulder	Lamb shoulder	Lamb liver	Lamb liver	Lamb kidney
Fat (%)	*14*	*3.3*	*3.6*	*4.5*	*15.3*	*18.2*	*7.1*	*6.8*	*3.7*
PCN 52/60	<0.20	0.06	<0.12	<0.15	0.35	<0.16	<0.18	<0.19	<0.07
PCN 53	<0.30	0.03	<0.07	<0.08	0.17	<0.09	0.12	<0.11	<0.02
PCN 66/67	0.11	0.04	0.02	0.13	2.24	0.64	0.08	2.91	0.15
PCN 68	<0.12	<0.01	<0.01	<0.01	0.08	<0.01	<0.02	<0.02	<0.01
PCN 69	<0.17	<0.01	<0.02	<0.02	0.04	<0.02	<0.02	<0.03	<0.01
PCN 71/72	<0.22	<0.01	<0.01	<0.02	0.02	<0.02	<0.02	<0.02	<0.01
PCN 73	<0.02	0.01	<0.01	0.1	2.38	0.12	0.04	1.56	0.05
PCN 74	<0.11	<0.01	<0.01	<0.01	0.08i	<0.01	<0.01	<0.02	<0.01
PCN 75	<0.02	0.01	<0.01	<0.01	0.33	<0.02	<0.02	<0.02	<0.01
Σ PCN*	**1.27**	**0.19**	**0.28**	**0.53**	**5.69**	**1.09**	**0.51**	**4.88**	**0.34**

* Sums of PCN are reported on an upper bound basis

Table 3b. Levels found in eggs and poultry

	Boneless chicken thighs	Fresh chicken Legs	Turkey breast	Medium free range hen eggs	Large free range hen eggs	Medium organic hen eggs	Large organic hen eggs	Free range duck eggs	Free range duck eggs
Fat %	*17.8*	*15.2*	*6.2*	*10.1*	*8.9*	*10.3*	*9*	*15*	*16.2*
PCN 52/60	0.95	0.50	0.14	0.49	0.90	0.44	1.25	0.36	4.67
PCN 53	0.20	0.19	0.10	0.23	0.25	0.25	0.76	<0.46	<0.43
PCN 66/67	0.13	0.13	0.13	0.09	0.21	0.12	0.15	0.13	0.70
PCN 68	0.05	0.17	0.02	0.15	0.21	0.07	0.11	<0.18	0.70
PCN 69	0.05	0.19	0.02	0.22	0.31	0.11	0.15	<0.26	0.81
PCN 71/72	0.03	0.18	0.02	0.14	0.3	0.09	0.17	<0.33	0.66
PCN 73	0.04	0.04	0.03	0.06	0.16	0.14	0.10	0.05	0.14
PCN 74	0.01	<0.01	<0.01	<0.01	0.04	0.03	0.03	<0.17	<0.16
PCN 75	<0.01	<0.01	0.01	<0.01	<0.02	<0.02	<0.02	<0.02	<0.02
Σ PCN*	**1.47**	**1.42**	**0.48**	**1.4**	**2.4**	**1.27**	**2.74**	**1.96**	**8.29**

* Sums of PCN are reported on an upper bound basis

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Table 3c. Levels found in fish and fishery products

	Cod fillet	Organic Scottish salmon fillets	Farmed salmon	Wild Atlantic salmon	Rainbow trout	Herring (2)	Sprats (2)	Eel (2)	Dressed Crab
Fat %	*0.6*	*13.8*	*11.7*	*9.0*	*5.5 / 6.9*	*17.6 / 24.1*	*21.6 / 23.2*	*30.7 / 39.1*	*7.4*
PCN 52/60	0.52	24.48	27.51	11.05	8.69 / 13.03	13.00 / 19.61	26.55 / 24.7	11.9 / 5.34	4.95
PCN 53	0.07	2.73	1.72	0.27	0.37 / 2.54	0.62 / <0.61	2.72 / 1.77	0.47 / 0.81	0.22
PCN 66/67	0.05	2.97	3.39	0.63	0.81 / 1.31	0.99 / 1.85	2.57 / 2.24	4.38 / 2.92	1.24
PCN 68	0.02	1.42	1.33	0.11	0.29 / 0.50	0.29 / 0.45	0.99 / 0.81	0.21 / 0.09	0.14
PCN 69	0.02	1.23	1.17	0.08	0.26 / 0.50	0.29 / 0.48	1.06 / 0.83	1.33 / 0.98	0.11
PCN 71/72	0.02	1.01	1.14	0.07	0.28 / 0.70	0.16 / <0.44	0.90 / 0.93	0.63 / 0.23	0.12
PCN 73	<0.01	0.44	0.82	0.03	0.09 / 0.12	0.13 / 0.22	0.43 / 0.38	0.28 / 0.21	0.04
PCN 74	<0.01	<0.20	0.18	0.01	0.02 / <0.16	0.02 / <0.23	<0.26 / <0.23	0.09 / 0.04	0.01
PCN 75	<0.01	<0.03	<0.03	<0.01	<0.02 / <0.02	<0.03 / <0.03	0.06 / 0.06	<0.04 / <0.04	<0.02
Σ PCN*	**0.73**	**34.51**	**37.29**	**12.26**	**10.83 / 18.88**	**15.53 / 23.92**	**35.54 / 31.95**	**19.33 / 10.66**	**6.85**

* Sums of PCN are reported on an upper bound basis

Table 3d. Levels found in dairy and other products

	Cows' milk (2)	Ewes' milk	English butter	Cheddar cheese	Cornish brie	Somerset brie	Cheese spread	Vegetable composite	Fruit composite	Bread composite	Pure cod liver oil
Fat %	*3.5 / 3.6*	*6.5*	*83.3*	*34.7 / 35.2*	*27.3*	*24.1*	*15.3*	*0.2*	*0.2*	*2.4*	*100*
PCN 52/60	0.03 / 0.03	0.09	0.86	0.17 / <0.32	<0.20	0.22	0.19	0.05	0.05	0.14	1.39
PCN 53	0.01 / 0.01	0.05	<0.44	<0.16 / <0.49	<0.12	0.07	<0.09	0.03	0.04	0.06	<0.11
PCN 66/67	0.08 / 0.06	0.25	1.79	0.33 / 0.13	0.26	0.26	0.51	0.01	<0.01	<0.01	0.32
PCN 68	<0.01 / <0.01	<0.01	0.11	<0.03 / <0.19	<0.02	0.02	0.03	<0.01	<0.01	<0.01	0.18
PCN 69	<0.01 / <0.01	<0.01	<0.43	<0.15 / <0.28	<0.03	<0.02	<0.09	<0.01	<0.01	<0.02	0.14
PCN 71/72	<0.01 / <0.01	<0.01	0.11	<0.04 / <0.35	<0.02	0.01	<0.02	<0.01	<0.01	0.01	0.19
PCN 73	0.05 / 0.04	0.08	2.06	0.17 / 0.03	0.13	0.12	0.91	<0.01	<0.01	<0.01	0.29
PCN 74	<0.01 / <0.01	<0.01	0.07	<0.03 / <0.19	<0.02	<0.01	0.03	<0.01	<0.01	<0.01	0.09
PCN 75	<0.01 / <0.01	<0.01	0.22	<0.03 / <0.03	<0.02	<0.02	0.04	<0.01	<0.01	<0.02	<0.08
Σ PCN*	**0.22 / 0.19**	**0.52**	**6.09**	**1.11 / 2.01**	**0.82**	**0.75**	**1.91**	**0.15**	**0.16**	**0.28**	**2.79**

* Sums of PCN are reported on an upper bound basis

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