POLYCHLORINATED NAPHTHALENES IN FOOD

Mortimer DN[1], Gem M[1], Rose M[2], White S[2], Fernandes A[2]

[1] Food Protection Division, Food Standards Agency, Aviation House, 125 Kingsway, London, WC2B 6NH, United Kingdom; [2] Central Science Laboratory, Department for Environment, Food and Rural Affairs, Sand Hutton, York, YO41 1LZ, United Kingdom

Introduction

Polychlorinated naphthalenes (PCNs) formerly had usages similar to those of polychlorinated biphenyls, and they can be produced in small amounts as combustion products[1]. However little work has been done on their presence in foods. Although they have been analysed in fish in several countries[2-4], this has usually been in the context of environmental monitoring, which has confirmed that the chemicals bioaccumulate, and only few surveys of fish as food have been carried out[5-6]. PCNs have been found to bioaccumulate in animals[7]. In Sweden they have been reported in human milk[8]. Some PCN congeners exhibit dioxin-like toxicity and systems of Toxic Equivalency Factors have been proposed[9-12]. At a European Food Safety Authority (EFSA) scientific colloquium on dioxins in 2004, it was concluded that compounds exhibiting dioxin-like toxicity should be considered for Toxic Equivalency Factors, but that this should be prioritised on the basis of exposure[13]. At present there is very little information on dietary exposure of humans to PCNs, although two surveys of foods have been carried out in Spain[5,14]. These showed that the highest concentrations were in fats and oils, cereals, fish, dairy products and meat. In the UK, the Food Standards Agency has been investigating the presence of PCNs in various foods.

Methods and materials

Samples

A total of 45 samples comprising mostly fish, meat and meat products, with smaller numbers of eggs, milk and milk products, fish oils, fruit and vegetables, were purchased in 2007. These samples were not intended to cover the food market comprehensively nor to represent the full United Kingdom diet but rather to enable a preliminary view to be formed of whether PCNs can be detected in the food chain.

Analysis

Samples were analysed by the Central Science Laboratory (CSL). 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 fish samples, the edible portions were the whole fish for sprats; the fish muscle less head, guts, bones and skin for herring and salmon.

The range of PCN congeners measured was intended to include those already reported to exhibit dioxin-like toxicity (PCNs 54, 56, 63, 66, 67, 68, 69 and 70), some that have been included in other work (PCNs 52, 60, 73 and 75) and any others that could be included within the same analytical methodology. In practice, the choice in such circumstances was limited by the availability of native internal standards of adequate purity, and the final list contained PCNs 52, 53, 66, 67, 68, 69, 71, 72, 73, 74 and 75. $^{13}C_{10}$ labelled PCNs 42, 52, 64 and 75 were added as internal standards.

CSL already had experience of analysing some of the PCNs of interest but for others the methodology required validation. This was achieved using samples of five different foods of both high and low fat contents, available following previous surveys carried out by CSL on behalf of the Food Standards Agency.

An aliquot of the prepared, homogenized sample was fortified with a known amount (in typically 50 µL) of $^{13}C_{10}$-labeled PCN internal standard mix. 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, 50 g of acid modified silica gel, 10 g of sodium sulphate 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 yield a 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 either one of two Micromass Autospec Ultima instruments fitted with a Hewlett Packard 6890N gas chromatograph and a CTC Analytics PAL GC

Table 1: Concentrations of PCNs in foods, 2007

Congener	**Concentrations (ng/kg fresh weight)**								
Sample Details	**Herring (*Clupea harengus*)**	**Rainbow trout (Oncor-hynchus mykiss)**	**Salmon fillets (*Salmo salar*)**	**Sprats (*Sprattus sprattus*)**	**Sprats (*Sprattus sprattus*)**	**Duck eggs**	**Duck eggs**	**Cheddar cheese**	**Sausages**
PCN 52	19.61	13.03	24.48	26.55	24.70	0.36	4.67	<0.32	0.01
PCN 53	0.32	2.54	2.73	2.72	1.77	<0.46	0.35	<0.49	0.03
PCN 66/67	1.85	1.31	2.97	2.57	2.24	0.13	0.70	0.13	0.11
PCN 68	0.45	0.50	1.42	0.99	0.81	0.04	0.70	<0.19	<0.12
PCN 69	0.48	0.50	1.23	1.06	0.83	<0.26	0.81	<0.28	<0.17
PCN 71/72	0.12	0.70	1.01	0.90	0.93	<0.32	0.66	<0.35	<0.22
PCN 73	0.22	0.12	0.44	0.43	0.38	0.05	0.14	0.03	<0.02
PCN 74	<0.23	0.04	0.09	<0.26	<0.23	<0.17	<0.16	<0.19	<0.11
PCN 75	0.02	<0.02	0.02	0.06	0.06	0.01	<0.01	0.01	<0.01

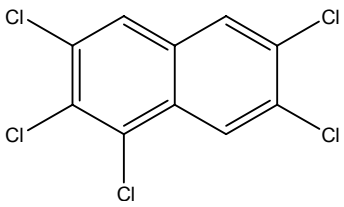
autosampler or a CTC A200S autosampler. Quantification was carried out on the basis of stable isotope dilution of the ^{13}C labelled surrogates (PCNs 42, 52, 64 and 75) and internal standardisation. The laboratory has taken part in a number of inter-laboratory trials for dioxins and non-*ortho* polychlorinated 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[16].

Results and discussion

Table 1 shows the concentrations of PCNs in the nine samples analysed so far. Some or all of the measured

PCNs were detected in all samples analysed. The highest concentrations were found in the fish samples. Much the most abundant congener in the fish samples was PCN 52, but in other food types this congener appears not to dominate to the same extent. The concentrations of the dioxin-like congeners were lower, with PCNs 66/67 being the most abundant in fish.

Structure of PCN-52



Because these results represent only a small number of samples taken from a narrow range of foods, it is not appropriate at this stage to attempt to estimate dietary exposures. Furthermore, there is insufficient toxicological information to fully understand the relevance to human health. As noted previously, TEF values for PCNs have been proposed in the literature[9-12]. However, it has not been possible to analyse all of the congeners mentioned, due to the non-availability of standards. In addition, there may be other adverse effects that would not be reflected in the TEF system. In order to determine whether

human dietary exposure to PCNs might be of toxicological significance, it will be important to gain a better understanding of levels in food and investigations will therefore continue.

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