RELATIVE CONTRIBUTION OF CHLORINATED NAPHTHALENES, - BIPHENYLS, - DIBENZOFURANS AND –DIBENZO-*P*-DIOXINS TO TOXIC EQUIVALENTS IN BIOTA FROM THE SOUTH COAST OF THE BALTIC SEA

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Introduction

Polychlorinated naphthalenes (PCNs) are industrial chemicals, which were commercially introduced in 1910. These compounds occur also as impurities in technical mixtures of polychlorinated biphenyls (PCBs) and are unintentionally formed during various processes such as copper ore roasting, aluminium smelting, waste incineration, *etc.* (1). Nearly 100 years after their first commercial synthesis, PCNs are found as widespread environmental contaminants world-wide (2-6). Environmental pollution by PCNs appears to be declining recently and peak concentrations of these compounds in the European environmental samples such as in sediment cores from inland England were in the 1960s (7). Nevertheless, the available database on congener-specific concentrations of CNs in different environmental matrices on a geographical basis is relatively small. There is no specific regulation on PCN production or usage worldwide and only in England there is a program to assess inventory and to dispose them safely. As indicated recently, relatively high loads of absolute concentrations of tri- to hexa-CNs in ambient air (3, 6) compared to much highly used PCBs suggest the existence of important and unidentified open sources of emission of PCNs to the atmosphere. Obviously, PCNs can still contribute to environmental problems at the local scale, especially at waste dump sites or point source areas (8). PCNs, like other compounds with dioxin-like activity have been deemed to be of the greatest possible significance to human and wildlife. However, there is no data available on the scale of dioxin-like activity contributed by PCNs when compared to others planar organochlorine compounds such as coplanar PCBs, PCDFs and PCDDs when they co-occur in biotic samples.

PCNs, PCBs, PCDFs and PCDDs were quantified recently in a set of marine samples from the southern part of the Baltic Sea and especially from the Gulf of Gdansk, Poland (2, 9-17). The area of the Gulf of Gdansk receives urban and agricultural runoff and domestic sewage effluents as well as industrial effluents. The aim of this study is to present the relative contribution of PCBs, PCNs, PCDFs and PCDDs to dioxin-like activities in marine biota from the Baltic Sea.

Key words: TCDD TEQs, PCNs, PCBs, PCDFs, PCDDs, Baltic Sea, sediments, plankton, mussel, crab, fish, cormorant, wildlife, seafood.

Materials and Methods

The methods used to quantify absolute concentrations of PCBs, PCNs, PCDFs and PCDDs have been given elsewhere (9, 16-17). Toxic equivalency factors (TEFs) used to calculate 2,3,7,8-tetrachlorodibenzo-*p*-dioxin (TCDD) equivalents of PCBs, PCNs, PCDFs and PCDDs are based on ethoxyresorufin-*O*-deethylase (EROD) or luciferase induction in the H4IIE rat hepatoma cell line (18-20). A few discrepancies exist in values of TCDD-TEF for some CN congeners in H4IIE-EROD and H4IIE-Luc tests (19-21). In this study, TEF value of the CN congener no. 40 was taken from Blankenship *et al.* (21), and for others from Hanberg *et al.* (19) and Villeneuve *et al.* (20), respectively. Since H4IIE-EROD TEF values of some congeners of chloronaphthalene nos. 67 and 73 differ as reported by Hanberg *et al.* (19) and Villeneuve *et al.* (20) – 2.8×10^{-4} and 2.0×10^{-3}, and 4.0×10^{-4} and 3.0×10^{-3}, the mean values of 1.14×10^{-3} and 1.7×10^{-3}, respectively, were used in this study to calculate TCDD TEQs of PCNs. Additionally, for the purpose of calculation of TEQs of co-eluting chloronaphthalene nos 33/34/37, 32/48, 66/67 and 64/68 (1, 2, 9-14) CNs, TEFs of 2.1×10^{-7}, 2.1×10^{-7}, 4.45×10^{-4} and 1.01×10^{-3} were assigned – based on the data from Hanberg *et al.* (19) and Villeneuve *et al.* (20). The concentrations of TCDD TEQs were determined based on an additive model from the concentrations of individual PCBs, PCNs, PCDFs and PCDDs.

Results and Discussion

TCDD-TEQs of non-*ortho* and mono-*ortho* PCBs, PCNs, PCDFs and PCDDs in biota from the southern part of the Baltic Sea are given in Table 1. Since there is still a lack of TCDD TEFs for many tetra- and penta-CNs which are quite abundant in biological samples examined as well as for 1,2,3,4,5,8-HxCN (no. 65) and 1,2,3,4,5,6,8-HpCN (no. 74), the calculated TCDD TEQs of PCNs are somewhat an underestimate of actual values. Another problem is the assignment of TEFs for co-eluting peaks for which only estimated TEQ values can be given. Only recently, it become possible to separate all isomers of pentachloronaphthalenes and hexachloronaphthalenes using Rt-βDEXcst phase capillary gas chromatography columns (22).

In terms of TCCD TEQs, chloronaphthalenes determined in the samples from the Baltic Sea are of the similar or higher importance as PCDDs (Table 1). Obviously, non-*ortho* and mono-*ortho* PCBs are the most important dioxin-like compounds contaminating seafood resources and wildlife from the southern part of the Baltic Sea followed by PCDFs. When based on TCDD TEQs calculated exclusively for PCNs and planar PCBs the contribution from chloronaphthalenes for such samples as plankton, blue mussel, crab, plankton feeding lesser sand eel and sand eel, and bottom feeding flounder is between 7.9-20.6%, 21.1-34.8%, 8.7%, 9.4-10 % and 8.2-20.3%, respectively. The contribution of PCNs to TCDD TEQs of all dioxin-like compounds quantified is between 2.6-2.9% for lesser sand eel and sand eel, 1.9-2.3% for three-spined stickleback, 4.4-4.6% for eelpout and lamprey, 6.2-12.3 for perch, 3.4% for pikeperch, 7.5-11.3% for flounder, 1.5% for harbour porpoise, and 1.4-1.6% for black cormorant.

In an earlier study of PCNs in three-spined stickleback and flounder from spatially different sites in the Gulf of Gdansk (2, 13) fish collected close to port harbour of the Gdynia in Oksywie and of the Gdansk in Westerplatte showed pattern of tetra-, penta- and hexa-CNs suggesting on existence of the local source of pollution with technical mixture of PCNs. Both the three-spined stickleback and flounder from the sites mentioned are also characterised by higher load of TCDD TEQs of PCNs when compared to fish from a more distant localities.

Table 1. TCDD Equivalents (H4IIE EROD or H4IIE-Luc) of dioxin-like PCBs, PCNs, PCDFs and PCDDs in various samples from the southern part of the Baltic Sea (pg/g lipid wt)

Sample and site/tissue	No.	PCBs	PCNs	PCDFs	PCDDs
Plankton - Gdansk Depth	1*	1.4	0.12	NA	NA
Plankton - Gotland Basin	1*	1.0	0.21	NA	NA
Plankton - Bornholm Basin	1*	1.0	0.26	NA	NA
Plankton - Pomeranian Bay	1*	2.2	0.28	NA	NA
Blue mussel - Gdynia	1*	7.5	2.0	NA	NA
Blue mussel - Orlowo	1*	3.0	1.6	NA	NA
Crab - Gdynia	1*	147.5	23.0	83.8	8.3
Lesser sand eel - Orlowo	1*	2.7	0.3	6.6	1.7
Sand eel - Orlowo	1*	2.9	0.3	6.3	0.8
Stickleback - Oksywie	1*	97.9	2.3	10.7	2.9
Stickleback - Redlowo	1*	100.0	0.6	13.2	1.5
Stickleback - North Port	1*	62.3	1.7	7.7	2.7
Stickleback - Górki Zachodnie	1*	68.2	1.1	NA	2.0
Herring - Gdynia	1*	17.0	1.5	NA	NA
Eelpout - Gdynia	1*	24.1	2.1	15.5	4.5
Lamprey - Gdynia	1*	44.6	1.1	NA	NA
Lamprey - Gdansk	1*	16.1	0.9	1.9	1.4
Perch - Gdynia	1*	189.1	1.5	12.0	3.5
Perch - Gdansk	1*	65.4	5.2	11.3	2.3
Cod - Gdynia	1*	2.6	1.4	5.8	1.1
Pikeperch - Gdynia	1*	20.3	1.2	7.6	6.0
Flounder - Gdynia	1*	132.3	11.8	9.5	3.9
Flounder - Gdansk	1*	64.6	7.2	10.1	2.2
Flounder - Mikoszewo	1*	10.6	2.7	7.9	2.6
Harbour porpoise – blubber**	4	5.3	0.3	12.8	1.5
Black cormorant – breast muscle**	3	529.9	9.8	41.2	52.0
Black cormorant – liver**	3	564.3	12.5	220.5	69.0

*Pooled samples; **Mean value; NA, not analysed

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