Bioaccumulation and Biomagnification Features of Polychlorinated Naphthalenes

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Abstract

There are a large differences in the pattern of PCNs retained in biota from various marine trophic levels. A lower trophic level organisms such as plankton and fish can bioconcentrate and bioaccumulate many chloronaphthalene congeners, and much less are biomagnified in animals higher in trophic level such as black cormorant and white-tailed sea eagle. In marine mammal such as harbour porpoise the BMF value greater then 1 was observed only for the pair of hexa-CNs, *i.e.* 1,2,3,4,6,7-/1,2,3,5,6,7-H_6CN (No. 66/67). Chloronaphthalene congeners, which do not have vicinal (adjacent) carbon atoms unsubstituted with chlorine (NVC-Cl PCNs) have BAF and BMF values higher than 1 in various animals. Some of the PCN congeners with two vicinal carbon atoms unsubstituted (DVC-Cl PCNs) are also bioaccumulated and biomagnified, while some other among the DVC-Cl PCNs, and also those members, which have from three to seven vicinal carbon atoms unsubstituted with chlorine on one or two rings potentially seem to be relatively easily metabolised and not retained in higher trophic level organisms.

Key words: Polychlorinated naphthalenes, PCNs, pollution, bioaccumulation, biomagnification, Baltic Sea, dioxin like compounds, fish, birds, marine mammals.

Introduction

Polychlorinated naphthalenes are a complex mixture of 75 congeners, which are a ubiquitous contaminants in the environment, and their main environmental sources identified are related to the technical PCN formulations, the technical PCB formulations, and thermal processes in the presence of chlorine [1]. The total world-wide production of PCNs from the above mentioned sources was roughly assessed for 150 000 tones (technical PCN), plus 100 tones (technical PCBs), plus 1-10 tones (thermal formation in this century) [2].

The molecule of naphthalene can be substituted with one to eight chlorine atoms. Up to 74 congeners of chloronaphthalene are formed in thermal processes, while a few are absent in technical PCN formulations such as the Halowax series [3]. Polychlorinated naphthalenes are a little studied environmental toxins, and many congeners have been identified and quantified recently in plankton, mussels, crab, fish, marine birds, birds of prey, marine mammals and sediment from the Baltic Sea [4-10].

Chloronaphthalenes are planar compounds. and beta-substituted members (2,3,6,7-substituted) are structurally analogous to planar PCBs and the most toxic dioxin and dibenzofuran congeners (PCDD/Fs).

Since some congeners of chloronaphthalene can occur in relatively high concentration in environmental matrices and so they may interfere during quantification of PCBs by typical gas chromatography with electron capture detection (GC/ECD). The method of choice in analysis of PCN homologues and congeners is high-resolution gas chromatography and electron-capture negative ionization mass spectrometry. Nevertheless, some isomers of tetra-, penta- and hexa-CN are coeluting in pair or triplicate even when separated using a long capillary columns gas chromatography. Since a perfect separation of the isomers is a crucial step in a study of environmental behaviour and bioaccumulation features of PCNs, a multi-dimensional capillary column gas chromatography coupled to mass spectrometer may in further offer the best possibility in analysis of that group of substances. There are many gaps in our knowledge on distribution, fate and impact of PCN homologues and congeners in the environmental compartments. and also on their toxicity.

In this study the bioaccumulation and biomagnification features of PCN in a several fish species. black cormorants. white-tailed sea eagles and harbour porpoise collected from the southern part of the Baltic Sea are summarised and evaluated.

Experimental Methods

Plankton. mussel (*Mytilus trosulus*). fish (eleven species), black cormorant (*Phalacrocorax carbo*). white-tailed sea eagles (*Haliaeetus albicilla*), harbour porpoise (*Phocoena phocoena*) and sediments were collected from the southern part of the Baltic Sea in 1991-1993. Polychlorinated naphthalenes were open tube extracted and cleaned-up using a nondestructive method with dialysis throughout a semipermeable polyethylene membrane with further fractionation on activated carbon column and final separation and quantification using capillary gas chromatography and high-resolution mass spectrometry (HRGC/HRMS). The concentrations of PCNs quantified in biological material were corrected for recovery using isotopically labelled 3,3',4,4',5-pentachlorobiphenyl (PCB no. 126) and 2,2',4,5,5'-pentachlorobiphenyl (PCB no. 101) as the internal and recovery standards, respectively. A detailed data on the concentrations of PCN homologues and congeners quantified in most of those matrices were presented elsewhere. including also the graphic presentation of the bioaccumulation and biomagnification potential of those substances in some of the animals studied [5-10]

Results and Discussion

It have been shown in an earlier works that the patterns of residual chloronaphthalene congeners found in the Baltic Sea biota can vary substantially among the species. Many a distinct peaks form the PCN congeners can be observed on HRGC/HRMS chromatograms of the extracts from the sediment, plankton. mussel, crab and some fish species, and usually only a few main in some predatory fish species and in a higher in their position in a food web animals such as black cormorant. white-tailed sea eagle and harbour porpoise [5-10].

A most abundant in the fingerprint of PCNs in sediment and in a lower food web animals are the congeners such as 1,3,5,7-T_4CN (No. 42), 1,2,4,6-/1,2,4,7-/1,2,5,7-T_4CN (Nos. 33/34/37), 1,4,6,7-T_4CN (No. 47), 1,2,3,5-/1,3,5,8-T_4CN (Nos. 28/43), 1,2,3,5-/1,3,5,8-T_4CN (No. 35), 1,2,3,5,7-/1,2,4,6,7-P_5CN (Nos. 52/60), 1,2,4,6,8-P_5CN (No. 61), 1,2,4,5,6-P_5CN (No. 57), 1,2,4,7,8-P_5CN (No. 62), 1,2,3,5,8-/1,2,3,6,8-P_5CN (Nos. 53/55) and 1,2,3,5,7,8-H_6CN (No. 69). In a higher food web animals such as marine birds and white-tailed sea eagles abundant are the PCN members such as 1,3,5,7-T_4CN (No. 42), 1,2,4,6-/1,2,4,7-/1,2,5,7-T_4CN (Nos. 33/34/37), 1,2,3,5,7-/1,2,4,6,7-P_5CN (Nos. 52/60), 1,2,4,6,8-P_5CN (No. 61) and 1,2,3,4,6,7-/1,2,3,5,6,7-H_6CN (No. 66/67), and 1,2,3,4,6,7-/1,2,3,5,6,7-H_6CN (No. 66/67), 1,2,4,6-/1,2,4,7-/1,2,5,7-T_4CN (Nos. 33/34/37), 1,2,5,8-/1,2,6,8-T_4CN, and a few other of tetra-CNs are relatively abundant also in harbour porpoise [5-10]. The patterns of PCNs quantified in a higher food web animals form the southern part of the Baltic Sea are also largely different when compared to that of the technical PCN mixtures such as Halowax 1014 and Equi-Halowax (an equivalent mixture of Halowax 1000, 1001, 1013, 1014, 1031, 1051 and 1099), or the pattern formed in fly ash and flue gas after incineration of the municipal solid wastes [3,11].

The fingerprints of PCNs in sediment and various biota with lower metabolic transformation capacity for those compounds can be indicative of the relative persistence of some chloronaphthalene congeners under abiotic environmental conditions and also of their dominance in sources of environmental pollution. Contrary, a relatively simplified PCN pattern in higher trophic level organisms is indicative of the structure dependent metabolism of those compounds.

The bioaccumulation (BAF) and biomagnification (BMF) factors of the congeners of chloronaphthalene from a lower to higher trophic level were calculated for a several marine species and are summarised in Table 1. The BAF and BMF values are indicative of the metabolic activity and related changes in the PCNs composition and will display the most stable structures. In fish such as herring, stickleback and sand eel/lesser sand eel when related to plankton the BAF values are higher then 1 for a most of PCNs quantified. In flounder, when related to blue mussel, the most retained are a few hexa- and hepta-CNs. The cormorants are able to metabolise many PCN congeners found in fish, and the most retained are a several members such as: Nos. 42 and 33/34/37 of tetra-, Nos. 52/60 and 58 of penta-, and Nos. 66/67 and 69 of hexa-CNs. The eagles can accumulate PCNs in high concentrations in their body [5]. Fish, both freshwater and marine, and waterfowl can be considered as a main prey species of the white-tailed sea eagles breeding at the coast of the Baltic Sea in Poland. Many tetra-, penta- and hexa-CNs, as well as both hepta-CNs are retained in the breast muscle and liver of white-tailed sea eagles when related to the concentrations determined in Baltic fish and black cormorants, their potential food items. In sea eagles an especially high BMF values were found for 1,3,5,7-T_4CN (No. 42), 1,2,3,5,7-/1,2,4,6,7-P_5CN (Nos. 52/60), 1,2,4,5,7-P_5CN (No. 58), 1,2,4,6,8-P_5CN (No. 61), 1,2,3,4,6-P_5CN (No. 50), 1,2,3,5,6-P_5CN (No. 51) and 1,2,3,4,6,7-/1,2,3,5,6,7-H_6CN (Nos. 66/67). In blubber of harbour porpoise, when related to herring, 1,2,3,4,6,7-/1,2,3,5,6,7-H_6CN (Nos. 66/67) showed highest BMF value, and all other PCN congeners were not retained by this marine mammal (Table 1).

The data of PCNs bioaccumulated in biota, from feed and water (fish) or only from feed (marine birds and marine mammals), clearly indicate that many congeners are metabolised and/or eliminated by higher trophic level animals. The congeners of chloronaphthalene, which do not have vicinal (adjacent) carbon atoms unsubstituted with chlorine (NVC-Cl PCNs) have BAF/BMF value higher than 1 in animals of different trophic level. There are 15 NVC-Cl PCNs: 1,3,5,7-T_4CN (No. 42), 1,2,3,5,7-P_5CN (No. 52), 1,2,4,5,7-P_5CN (No. 58), 1,2,4,6,7-P_5CN (No. 60), 1,2,4,6,8-P_5CN (No. 61), 1,2,3,4,5,7-H_6CN (No. 64), 1,2,3,4,6,7-H_6CN (No. 66), 1,2,3,5,6,7-H_6CN (No. 67), 1,2,3,5,6,8-H_6CN (No. 68), 1,2,3,5,7,8-H_6CN (No. 69), 1,2,4,5,6,8-H_6CN (No. 71), 1,2,4,5,7,8-H_6CN (No. 72), 1,2,3,4,5,6,7-H_7CN (No. 73), 1,2,3,4,5,6,8-H_7CN (No. 74) and

Table 1

Bioaccumulation (BAF) and biomagnification (BMF) factors of chloronaphthalene congeners in the marine food webs

PCN no.	Structure	Pl/H	Pl/St	Pl/Se	M/F	F/C_m	F/C_l	F/E_l	F/E_m	C_l/E	C_m/E	H/H_p
Tetrachloronaphthalenes												
42	1,3,5,7-T_4CN	7.6	28	5.9	0.93	27	37	95	56	5.2	7.4	0.03
33/34/37	1,2,4,6-/1,2,4,7-/1,2,5,7-T_4CN	1.7	3.0	2.1	0.17	4.4	5.1	12	7.7	2.9	3.0	0.14
44	1,3,6,7-T_4CN	0.18	18	5.3	0	0.17	0.16	16	9.8	4.9	2.8	NA
47	1,4,6,7-T_4CN	2.8	5.7	2.3	0.13	0.29	0.34	4.9	2.8	19	12	0.08
36/45	1,2,5,6-/1,3,6,8-T_4CN	1.2	5.2	0.74	0.09	0.13	0.13	15	7.1	3.7	3.0	0.18
28/43	1,2,3,5-/1,3,5,8-T_4CN	1.7	4.7	2.2	0.10	0.24	0.35	15	0.86	0.41	3.1	0.13
27/30/39	1,2,3,4-/1,2,3,7-/1,2,6,7-T_4CN	1.3	3.5	1.0	0.06	0.08	0.13	5.1	3.4	2.9	4.4	0.18
32/48	1,2,4,5-/2,3,6,7-T_4CN	2.8	7.0	1.6	0.18	0.05	0.07	4.5	1.2	4.5	2.3	0.11
35	1,2,4,8-T_4CN	4.3	5.5	3.0	0.23	0.44	0.43	0.48	0.42	0.81	0.95	0.06
38/40	1,2,5,8-/1,2,6,8-T_4CN	0.7	1.8	0.89	0.04	0.34	0.41	0.61	0.73	0.62	1.6	0.32
46	1,4,5,8-T_4CN	1.2	1.8	0.57	0.07	0.12	0.15	0.26	0.32	0.50	1.4	0.14
41	1,2,7,8-T_4CN	0.4	1.2	0.2	0.03	0.01	0.11	1.0	1.2	0.15	3.8	0.38
Pentachloronaphthalenes												
52/60	1,2,3,5,7-/1,2,4,6,7-P_5CN	16	43	10	1.5	27	37	10	69	22	18	0.03
58	1,2,4,5,7-P_5CN	13	19	7.2	2.0	4.4	5.1	21	15	3.2	2.7	0.02
61	1,2,4,6,8-P_5CN	13	8.4	5.6	1.5	0.17	0.16	46	30	6.9	5.5	0.02
50	1,2,3,4,6-P_5CN	3.2	8.4	5.1	0.37	0.29	0.34	150	54	22	11	0.11
51	1,2,3,5,6-P_5CN	2.1	16	4.7	0.23	0.13	0.13	64	13	26	4.8	0.84
54	1,2,3,6,7-P_5CN	11	25	4.6	0.14	0.24	0.35	36	9	4.6	1.6	0.07
57	1,2,4,5,6-P_5CN	8.3	12	6.2	1.2	0.08	0.13	11	7.8	5.7	3.6	0.02
62	1,2,4,7,8-P_5CN	8.7	7.1	7.7	0.47	0.05	0.07	17	11	3.8	2.6	0.01
53/55	1,2,3,5,8-/1,2,3,6,8-P_5CN	6.7	5.2	5.1	0.44	0.44	0.43	2.5	1.0	4.7	2.6	0.02

Table 1, cont'd

Table 1. continued

PCN no.	Structure	Pl/H	Pl/St	Pl/Se	M/F	F/C_m	F/C_l	F/E_l	F/E_m	C_l/E	C_m/E	H/H_p
Pentachloronaphthalenes												
59	1,2,4,5,8-P_5CN	8.1	4.3	4.0	0.50	0.34	0.41	0.51	0.36	6.3	0.64	0.01
49	1,2,3,4,5-P_5CN	7.1	7.1	4.1	0.28	0.12	0.15	4.5	0.89	28	1.5	0.01
56	1,2,3,7,8-P_5CN	7.5	6.0	4.3	0.14	0.01	0.11	0.73	2.6	6.3	6.2	0.01
Hexachloronaphthalenes												
66/67	1,2,3,4,6,7-/1,2,3,5,6,7-H_6CN	11	10	2.8	3.3	7.0	7.1	45	37	2.2	3.0	1.2
64/68	1,2,3,4,5,7-/1,2,3,5,6,8-H_6CN	16	5.9	3.5	4.7	0.92	0.52	1.9	1.8	0.48	0.39	0.02
69	1,2,3,5,7,8-H_6CN	21	5.6	3.2	16	1.9	1.4	0.84	0.90	0.17	0.18	0.17
71/72	1,2,4,5,6,8-/1,2,4,5,7,8-H_6CN	21	2.9	2.4	6.3	0.95	0.54	0.50	0.41	0.28	0.19	0.01
63	1,2,3,4,5,6-H_6CN	11	6.2	3.1	1.4	0.15	0.11	1.4	1.1	0.51	0.37	0.06
65	1,2,3,4,5,8-H_6CN	24	5.7	9.8	2.2	0.03	0.01	0.41	0.27	0.85	0.46	0.01
Heptachloronaphthalenes												
73	1,2,3,4,5,6,7-H_7CN	3.1	0.43	0.31	2.6	0.09	0.08	2.6	0.84	0.43	0.20	0.62
74	1,2,3,4,5,6,8-H_7CN	2.8	0.33	0.10	2.1	0.02	0.04	5.7	1.8	1.1	0.71	0.73

Pl/H (plankton to herring)
Pl/St (plankton to stickleback)
Pl/Se (plankton to sand eel and lesser sand eel)
M/F (mussel to flounder)
F/C_m (fish to black cormorant; breast muscle)
F/C_l (fish to black cormorant; liver)
F/E_l (fish to white-tailed sea eagle; breast muscle)
F/E_m (fish to white-tailed sea eagle; liver)
C_l/ E (liver of cormorant to white-tailed sea eagle; breast muscle)
C_m/E (breast muscle of cormorant to white-tailed sea eagle; breast muscle)
H/H_p (herring to harbour porpoise)
NA (not analysed)

1,2,3,4,5,6,7,8-O_8CN (No. 75). Chloronaphthalene congeners, which have two vicinal carbon atoms unsubstituted with chlorine on one or both napththalene rings (DVC-Cl PCNs) seem to be also relatively resistant to metabolism by animals, while those with more then two vicinal carbon atoms unsubstituted are more easily metabolised or eliminated.

All eight isomers of penta-CNs with two vicinal carbon atoms unsubstituted with chlorine, such as nos. 50, 51, 53, 54, 55, 57, 59 and 62 are bioaccumulated by herring, and most of them also by black cormorant and sea eagle. The isomers of penta-CN such as no. 59 (unsubstituted at adjacent $\beta\beta$ positions), nos. 53/55 (unsubstituted at adjacent $\beta\beta$ positions and α/α positions, respectively) are not biomagnified in black cormorant and sea eagle. Also two isomers of penta-CN, which have three vicinal carbon atoms unsubstituted with chlorine (TVC-Cl PCNs) at one ($\alpha\beta\beta$ positions - No. 49) or two rings ($\alpha\alpha\beta$ positions - No. 56) are not biomagnified by black cormorant and sea eagle.

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