Chloronaphthalenes in stickleback *Gasterosteus aculeatus* from the southwestern part of the Gulf of Gdańsk, Baltic Sea

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1. Introduction

Chloronaphthalenes (CNs; PCNs) represent a complex mixture of 75 congeners, which are ubiqitous environmental pollutants. Many tetra- through hepta-CNs have been identified and/or quantified recently in sediment and organisms of different trophic levels from the Baltic Sea [1-7]. Together 74 off 75 possible CN members were identified in a flue gas, fly ash and circulating water samples of the MSWI [9-10]. 1,3,6,7-T4CN (no. 44) and 1,2,3,6,7-P5CN (no. 54), which were not reported in a technical Halowax formulations but are formed during combustion processes [8,10], were found in sediment, plankton and higher in their position in a trophic web animals from the Baltic Sea [1-6].

The aim of this study is to examine concentrations, spatial distribution and patterns of CNs in a coastal area of the Gulf of Gdańsk using sticklebacks as a biological matrix.

2. Materials and Methods

30 sticklebacks *Gasterosteus aculeatus* of both sexes were collected from every site examined in the beach zone in the southwestern part of the Gulf of Gdańsk from June 2 - July 1, 1996 (Figure 1).

The analytical method used for the determination of CNs is a part of a multi-residue procedure of many OCs and PAHs, and was explained in detail in other papers [1-4,6]. The nondestructive extraction and cleanup procedures were performed. After split of the analyte a 90% part was further cleaned up on silica column and than HPLC fractionated on activated carbon column. A final CNs identification and quantification was acomplished using HRGC/HRMS. $^{13}C_{12}$ - 3,3',4,4',5-pentachlorobiphenyl (CB no. 126), $^{13}C_{12}$ - 2,2',4,5,5'-pentachlorobiphenyl (CB no. 101), native CNs nos. 66/67, 71 and 73 and technical Halowax 1014 were analytical standards used to control recovery as well as elution order, identification and quantification of CNs in an analyte.

3. Results and Discussion

The sticklebacks collected near the harbours of the sea port complex of the city of Gdynia (Oksywie site) contained relatively a largest concentration of the total CNs (Table 1). The sticklebacks taken close to the harbour of the North Port of the city of Gdańsk and those from the sea side area under Pleniewo (Górki Zachodnie site; near the Brave Vistula outlet from the Dead Vistula Channel) contained comparable concentrations of the total CNs, while fish from the Redłowo site was less contaminated.

In sticklebacks from all sampling sites tetra-CNs were a dominating homologue group (52-

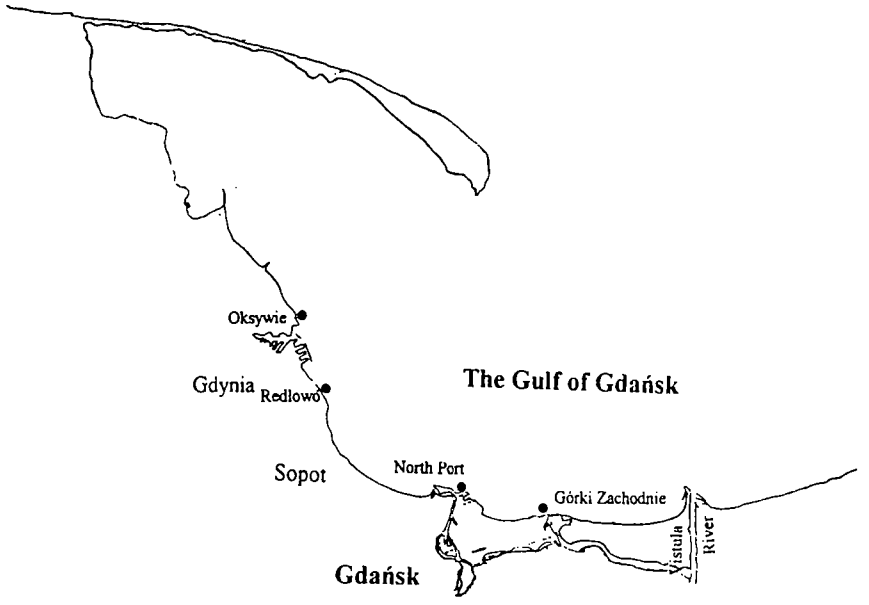

Figure 1. Map of the sampling sites (•) of sticklebacks.

61%) and followed by penta- (38-46%), hexa- (1.0-1.6%) and hepta-CNs (0.01-0.04%) (Figure 2). A composition (%) of tetra- through hepta-CNs in technical mixture of Halowax 1014 is totally different from that observed in sticklebacks.

1,2,3,5,7-/1,2,4,6,7-P5CN (nos. 52/60), 1,2,4,6-/1,2,4,7-/1,2,5,7-T4CN (nos. 33/34/37) and 1,3,5,7-T4CN (no. 42) are the most contributing CN congeners in sticklebacks. These CNs are only a trace (no. 42) or relatively less contributing (≤5%) members in Halowax 1014. Some other CNs, which are also important due to their notable contribution (up to ~10%; depending on the sampling site), are members such as 1,2,4,6,8-P5CN (no. 61), 1,4,6,7-T4CN (no. 47), 1,2,3,5-/1,3,5,8-T4CN (nos. 28/43), 1,2,4,8-T4CN (no. 35), 1,2,5,8-/1,2,6,8-T4CN (nos. 38/40), 1,2,4,5,6-P5CN (no. 57) and 1,2,4,7,8-P5CN (no 62).

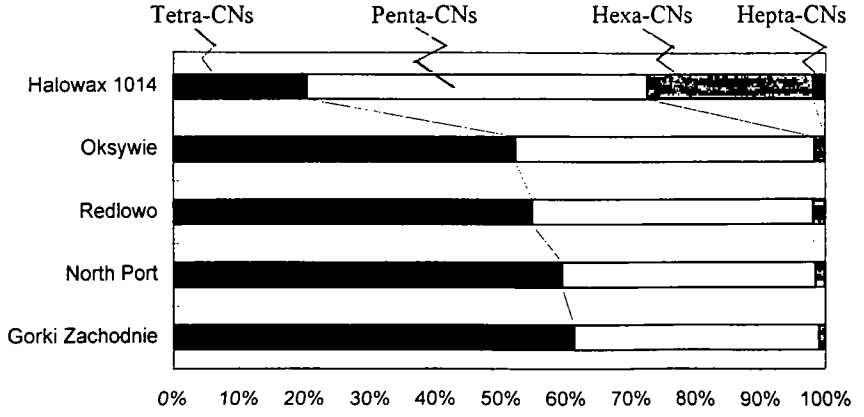

Figure 2. Chloronaphthalene composition (%) of Halowax 1014 and sticklebacks.

Tabie 1
Concentrations of CNs in Stickleback (ng/g Lipid Wt) from the Gulf of Gdańsk

		Sampling site, date and lipid content (%)			
		Górki Zachodnie June 2 '92	North Port July 1 '92	Redłowo June 3 '92	Oksywie June 15 '92
PCN no.	Structure	2.44 (%)	2.66	2.38	2.44
Tetrachloronaphthalenes					
42	1,3,5,7-T4CN	13	12	4.2	11
33/34/37	1,2,4,6-/1,2,4,7-/1,2,5,7-T4CN	13	15	4.7	17
44	1,3,6,7-T4CN	0.5	0.4	0.2	0.3
47	1,4,6,7-T4CN	5.7	4.8	2.2	5.3
36/45	1,2,5,6-/1,3,6,8-T4CN	0.61	0.58	0.21	0.51
28/43	1,2,3,5-/1,3,5,8-T4CN	5.3	6.2	2.0	7.1
27/30/39	1,2,3,4-/1,2,3,7-/1,2,6,7-T4CN	0.93	0.99	0.34	1.1
32/48	1,2,4,5-/2,3,6,7-T4CN	0.79	0.72	0.25	1.3
35	1,2,4,8-T4CN	3.4	4.6	1.2	7.3
38/40	1,2,5,8-/1,2,6,8-T4CN	3.0	4.1	1.2	5.2
46	1,4,5,8-T4CN	1.4	2.3	0.53	3.6
41	1,2,7,8-T4CN	0.14	0.17	0.051	0.32
Total tetra-CNs		**48**	**52**	**17**	**60**
Pentachloronaphthalenes					
52/60	1,2,3,5,7-/1,2,4,6,7-P5CN	17	15	7.8	19
58	1,2,4,5,7-P5CN	1.0	1.3	0.32	1.6
61	1,2,4,6,8-P5CN	4.1	5.9	1.6	11
50	1,2,3,4,6-P5CN	0.81	1.4	0.56	1.6
51	1,2,3,5,6-P5CN	0.60	0.73	0.38	0.87
54	1,2,3,6,7-P5CN	0.44	0.22	0.25	0.34
57	1,2,4,5,6-P5CN	2.0	2.9	0.87	5.6
62	1,2,4,7,8-P5CN	1.4	3.3	0.74	5.7
53/55	1,2,3,5,8-/1,2,3,6,8-P5CN	1.0	1.4	0.55	2.6
59	1,2,4,5,8-P5CN	0.99	1.7	0.37	4.2
49	1,2,3,4,5-P5CN	0.13	0.19	0.070	0.41
56	1,2,3,7,8-P5CN	0.041	0.09	0.026	0.12
Total penta-CNs		**30**	**34**	**14**	**53**
Hexachloronaphthalenes					
66/67	1,2,3,4,6,7-/1,2,3,5,6,7-H6CN	0.45	0.40	0.37	0.59
64/68	1,2,3,4,5,7-/1,2,3,5,6,8-H6CN	0.096	0.22	0.058	0.30
69	1,2,3,5,7,8-H6CN	0.13	0.35	0.082	0.47
71/72	1,2,4,5,6,8-/1,2,4,5,7,8-H6CN	0.062	0.19	0.032	0.29
63	1,2,3,4,5,6-H6CN	0.044	0.12	0.026	0.14
65	1,2,3,4,5,8-H6CN	0.011	0.063	0.015	0.096
Total hexa-CNs		**0.79**	**1.3**	**0.58**	**1.9**
Heptachloronaphthalenes					
73	1,2,3,4,5,6,7-H7CN	0.0032	0.013	0.007	0.030
74	1,2,3,4,5,6,8-H7CN	0.004	0.0081	0.004	0.017
Total hepta-CNs		**0.0072**	**0.021**	**0.011**	**0.047**
Total PCNs		**78**	**87**	**31**	**120**

There are characteristic patterns formed by the tetra-, penta- and hexa-CNs in sticklebacks from the particular sampling sites (Figures 3-5).

The sticklebacks collected from the North Port and Oksywie sites show a similar pattern of tetra-CNs (Figure 3). In both those samples CN nos. 33/34/37 are slightly more abundant members than CN no. 42, and an opposite situation is observed for the sticklebacks from the Górki Zachodnie and Redłowo sites. Nevertheless, the pattern of tetra-CNs found in sticklebacks from the Redłowo site is very similar to that of Górki Zachodnie site.

Also the pattern of penta- and hexa-CNs is very similar for sticklebacks taken from the North Port and Oksywie on one side, and for fishes from the Górki Zachodnie and Redłowo sampling sites, on the other (Figures 4 and 5). The fishes from the North Port and Oksywie sites show a larger abundance of the PCN no. 61, when compared to both other sites. In sticklebacks from the North Port and Oksywie sites hexa-CNs such as CN nos. 64/68, 69 and 71/72 are much more abundant members than in fishes from the Górki Zachodnie and Redłowo sites.

1,2,6,7-T4CN (no. 29), 1,2,3,6,7-P5CN (no. 54), 1,2,3,6,8-P5CN (no. 55) and 1,2,3,6,7,8-H6CN (no. 70) were not found in Halowax 1014 [10]. Also 1,3,6,7-T4PCN (no. 44) was not observed on the HRGC/HRMS chromatogram of the equivalent mixture of Halowax 100, 1001, 1013, 1014, 1031, 1051 and 1099 [8]. Both CN no. 44 and 54, which are formed during combustion, were found in stickleback examined, while CN nos. 29, 55 and 70 remained undetected in those fishes (Table 1). Chloronaphthalenes, which have no vicinal carbon atoms unsubstituted with chlorine (NVC-Cl CNs), such as nos. 42, 52, 60 and 61 are the most abundant members in a bulk of CNs in sticklebacks. The other NVC-Cl CNs, such as nos. 58, 64, 66, 67, 68, 69, 71, 72, 73 and 74 were found in small concentration in sticklebacks but are known to be bioaccumulated (BAF) in fishes, and biomagnified (BMF) in black cormorants and harbour porpoise [1,4,5]. Chloronaphthalenes with two (DVC-Cl CNs) or three vicinal carbon atoms unsubstituted with chlorine (TVC-Cl CNs), such as nos. 33, 34, 35, 37, 47, 53, 55, 57, 59 and 62, are also relatively abundant congeners in stickleback but their BAF (when considering a food as a main route of the intake) in fishes and BMF

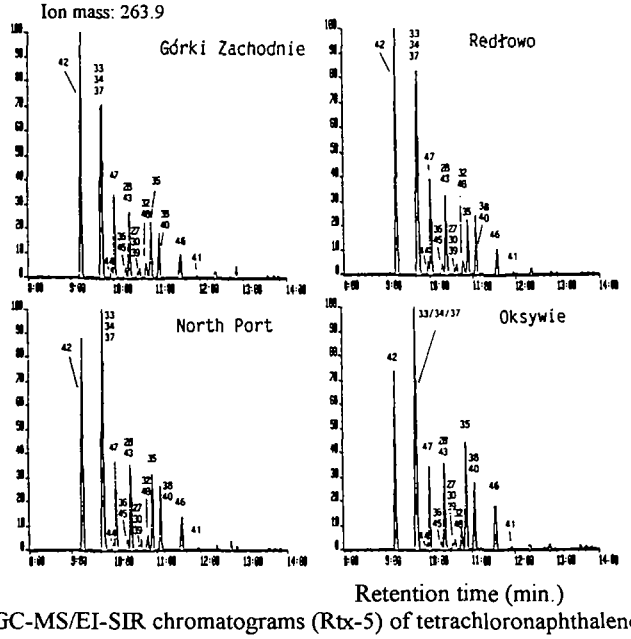

Figure 3. HRGC-MS/EI-SIR chromatograms (Rtx-5) of tetrachloronaphthalenes in sticklebacks (details of the peaks numbering are explained in Table 1).

values in fish-eating marine mammals and birds, are usually less than 1 [1,4,5]. Some of DVC-Cl CNs such as nos. 50, 51, 54, 63 and 65, as well as such TVC-Cl CNs as nos. 49 and 56 are well resolved on the Rtx-5 capillary column as a single peaks, and all are only minor constituents in total CNs in sticklebacks. One TVC-Cl CN, *i.e.* congener no. 35 is relatively abundant in total PCNs detected in sticklebacks and seems to be the most persistent in that group of CNs. Another important contributon is from two pairs, each containing one TVC-Cl -CN and one DVC-Cl CN, *i.e.* from the pair formed by TVC-Cl CN (no. 28)/DVC-Cl CN (no. 43), and by double DVC-Cl CN (no. 38)/TVC-Cl CN (no. 40). 1,2,5,8T4CN (no. 38) has two pairs of vicinal carbon atoms unsubstituted with chlorine, so was colled double DVC-Cl CN (DDVC-Cl CN). Without a satisfactory the HRGC separation of all CN members as a single peaks or without an apropriate knowledge on their structure related differences of the physicochemical properties, it is rather difficult to forecast, which of the DVC-Cl/DDVC-Cl or TVC-Cl CN congeners found in a double or triplicate peaks is the most persistent. Chloronaphthalenes with four vicinal carbon atoms unsubstituted with chlorine (QVC-Cl CNs), such as no. 41, and also DDVC-Cl CN no. 46, were usually less abundant members in fishes examined. Another QVC-Cl CN, namely congener no. 27 coelutes together with two TVC-Cl CNs nos. 30 and 39, while third QVC-Cl CN member, *i.e.* no. 31, was not detected.

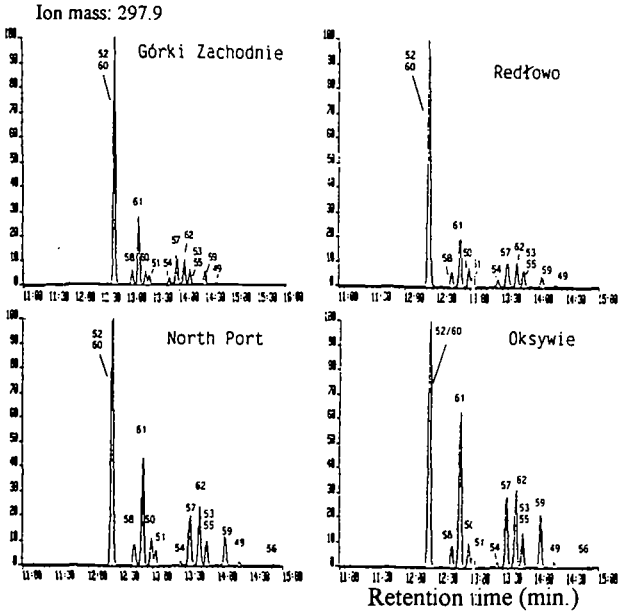

Figure 4. HRGC-MS/EI-SIR chromatograms (Rtx-5) of pentachloronaphthalenes in sticklebacks (details of the peaks numbering are explained in Table 1).

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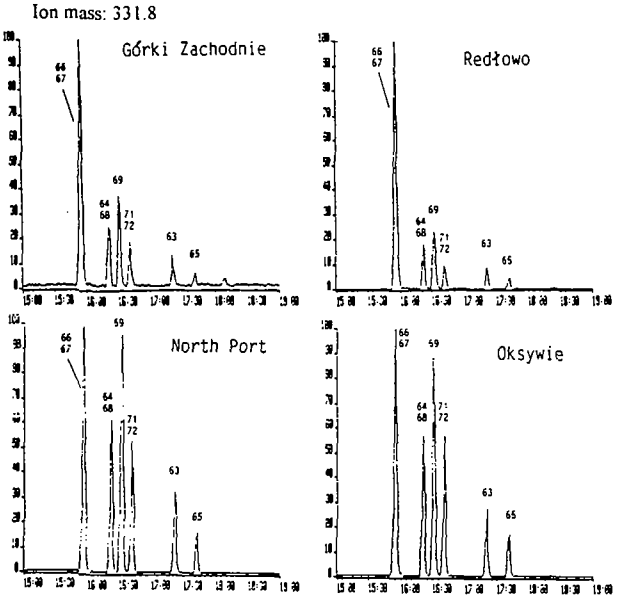

Figure 5. HRGC-MS/EI-SIR chromatograms (Rtx-5) of hexachloronaphthalenes in sticklebacks (details of the peaks numbering are explained in Table 1).

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