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Influence of Smoking on Indicatory PCB Congeners Residues Levels in Fish Slices

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Key words: smoking, herring, mackerel, indicatory PCB congeners

The aim of this study was do determine changes in concentrations of indicatory PCB congeners (IUPAC numbers: 28, 52, 101, 118, 153, 138, 180) during industrial hot smoking of mackerel (*Scomber scombrus* L.) and herring (*Clupea harengus* L.) slices and cold smoking of mackerel slices. PCB content in raw mackerel slices averaged from 1.32±0.29 ng/g wet w. for PCB 52 to 4.66±0.72 ng/g wet w. for PCB 153. In herring slices, PCB content ranged from 1.36±0.25 ng/g wet w. for PCB 28 to 16.50±1.94 ng/g wet w. for PCB 153. During hot smoking, losses of the examined compounds were observed – in herring slices by 15% (PCB 153) to 32% (PCB 52), while in mackerel slices by 3.7% (PCB 80) to 38% (PCB 28). Simultaneously, a slight increase in the content of PCB 180, PCB 118, PCB 153, PCB 138 and PCB 101 occurred during the proper smoking, between 1.5th and 2.5th hour of the smoking process. During cold smoking (26°C, 8 h), PCB concentrations increased significantly ($p<0.05$) by 26% (PCB 28, PCB 138) to 43% (PCB 180). In the final stage of smoking, PCB content in the alder sawdust and in the smoke had a significant effect on the levels of the analysed PCB congeners in the smoked slices. The main parameter determining the change of these compounds contents was their decrease in co-distillation with steam. In the final phase of the hot smoking a little increase of PCB compounds contents was a consequence of their penetration with smoke to the fish meat tissue.

INTRODUCTION

Fish from the Baltic and Norwegian Seas constitute a considerable percentage of fish appreciated by Polish consumers. Apart from valuable nutrients, the fish may also contain chloroorganic pollutants such as polychlorinated biphenyls that accumulate in human adipose tissue. Their levels in human adipose tissue in Poland were similar to those reported for industrialized nations of Western Europe [Loganathan *et al*., 1993; Czaja *et al*., 1999] and averaged 1500 ng/g lipids. Recent studies have indicated that the exposure to contaminants, such as PCBs, may cause disruption in reproductive function, and contribute to neurobehavioral and developmental deficits in newborns and young children [Sager, 1983; Courval *et al*., 1996; Yang *et al*., 2005]. Also Mergler *et al*. [1998] have reported neurotoxic effects in adults exposed to, *inter alia*, PCBs. These symptoms were the result of environmental exposure *via* fish consumption.

Especially high bioaccumulation indices of persistent organic pollutants (including PCBs) were reported for fish and other aquatic animals [Ciereszko & Witczak, 2002; Ciereszko *et al*., 2004; Tomza *et al*., 2006; Witczak & Leszczyńska, 2006; Szlinder-Richert *et al*., 2009]. The toxicological evaluation of raw fishery materials needs to be completed by the analysis of the effects of processing that may lead to reduction or even total elimination of toxic compounds from the final products. Smoking is one of the methods of food processing commonly used for years, not only in Poland [Usydus *et al*., 2009; Polak-Juszczak, 2008].

Taking into consideration the rate of fish consumption in Poland, the aim of this study was do determine changes in concentrations of indicatory PCB congeners during industrial hot smoking of mackerel (*Scomber scombrus* L.) and herring (*Clupea harengus* L.) slices and cold smoking of mackerel slices. Indicator PCBs are the target congeners (IUPAC numbers: 28, 52, 101, 118, 153, 138, 180) recommended by the European Union for assessing the pollution by PCBs [Commission of the European Communities, 1999]. This paper is supplementary to the studies published by Witczak & Ciereszko [2006, 2008].

MATERIALS AND METHODS

The material for analysis consisted of frozen double slices of herring and mackerel. The fish were harvested from the Norwegian Sea, and after one-month storage at a temperature -18°C were subjected to smoking. Alder sawdust was used for smoke production.

Smoking was carried out under industrial conditions in an "Atmos" type smoking chamber [Witczak & Ciereszko, 2006]. The chamber provided automatic temperature and humidity control, and had a forced air circulation heating system.

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Prior to hot smoking, the herring and mackerel slices were brined for 3 min in a 15% NaCl solution. Prior to cold smoking, the mackerel slices were brined for 3 h in a 15% NaCl solution with spices: bay leaves, allspice, paprika and mustard seeds.

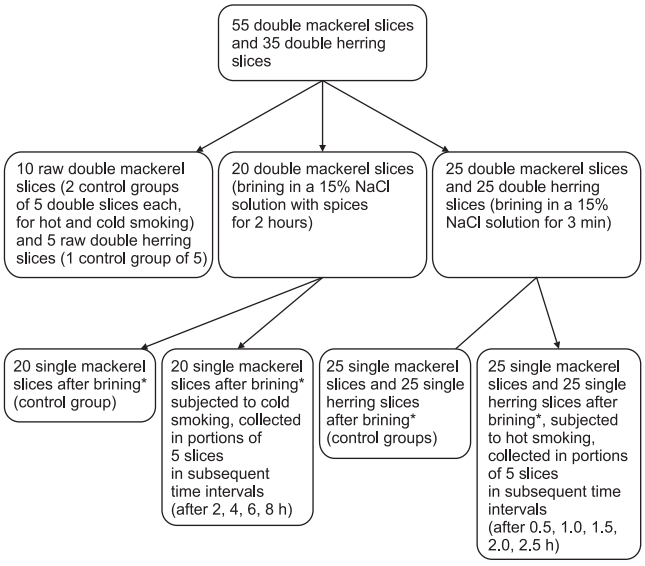
To determine changes during brining, 5 additional slices were split longitudinally into single slices, of which some served as the control and others were brined (Figure 1).

Two smoking methods were applied:

1. hot smoking – the slices were prepared according to the diagram (Figure 1). Fish slices intended for hot smoking were dried at 40°C for 1 h, and next the proper smoking started, during which the smoke was supplied into the smoking chamber and the temperature was gradually raised to 80°C. Samples for analysis were collected after: 0.5, 1.0, 1.5, 2.0 and 2.5 h. Additionally, absorbent paper strips soaked in soybean oil were placed among the mackerel slices on the upper bars of the smoking chamber. The paper strips measured 28 cm × 7 cm, so their surface area was similar to an average surface area of a single mackerel slice (196 mL). The smoking chamber contained two smoking trolleys (120 kg of raw material). Alder sawdust consumption amounted to 20 kg/smoking cycle.
2. cold smoking – the slices were prepared according to the diagram (Figure 1). Smoking was conducted at 25–26°C for 8 h. Samples for analysis were collected after: 2, 4, 6 and 8 h. The smoking chamber contained two smoking trolleys (160 kg of raw material). Alder sawdust consumption amounted to 40 kg/smoking cycle.

To determine which PCB congeners penetrated from the sawdust to the smoke, a dry distillation of alder sawdust directly to *n*-hexane was conducted in laboratory conditions. Each time the condenser was rinsed with *n*-hexane, which was next added to the sample.

Some samples were fortified with a known amount of each of the seven PCB congeners to enable proper identification of the examined compounds and to determine recoveries. For this reason, additionally the Pesticides Surrogate Spike Mix



* divided along a dorsal line

FIGURE 1. A diagram of the experiment.

was applied, which is an acetone solution of decachlorobiphenyl and 2,4,5,6-tetrachloro-m-xylene (Chlorinated Pesticides Mix, SUPELCO, No 4–9151). For quantitative analysis, an isooctane solution of seven indicatory PCB congeners (N0813; Promochem GmbH, Germany) was used.

For PCB analysis, the slices were deskinned, minced, and homogenised, sampling thereafter three times 30-g weighted amounts each of the muscle tissue (three replications). As a substitute reference material, a "chlorobiphenyls in mackerel oil" no. 350 (Promochem GmbH, Wesel, Germany), which included seven indicatory congeners (PCB IUPAC No: 28, 52, 101, 118, 138, 153, 180) was used. The samples were dried and comminuted in a mortar with anhydrous Na_2SO_4 (roasted at 400°C for 4 h) until uniform dry matter had been obtained. To extract the PCBs together with lipids, a 50 mL acetone/*n*-hexane solution (v/ v) (2.5:1) was used each time, followed by a 50 mL *n*-hexane/diethyl ether solution (v/v) (9:1). After filtration, the combined extracts were concentrated in a vacuum rotary evaporator. Thereafter, the extracts were transferred quantitatively into 10 mL weighted glass test tubes. These test tubes had been previously cleaned three times with *n*-hexane/acetone solution (v/v) (3:1) in the ultrasound rinser. The solvent was evaporated under a nitrogen atmosphere, and residues were desiccated at 60°C to constant weight. The lipid content was determined according to a gravimetric method. The analysis for the content of PCBs was continued by dissolving again 0.5 g of the obtained fat in *n*-hexane to 2 mL. The samples were purified by adding 6 mL of fuming H_2SO_4 [7% SO_3 in concentrated H_2SO_4 (w/w)]. After separation of layers, the upper layer was transferred quantitatively into a dry test tube, rinsed several times with deionized water, and then dried in 8 mL Li-Chrolut columns on an anhydrous Na_2SO_4 bed. The samples were concentrated in a vacuum rotary evaporator to 0.1 mL, placed in the glass insert (0.2 mL) of screw-cap vials (1 mL), and stored at -5°C for analysis. The analysis was performed by gas chromatography (GC) coupled with mass spectrometry (MS) on a GC-MS (HP 6890/5973) apparatus. A HP-5, 5% phenyl methyl siloxane (30 m i.d., 250 µm, 0.25 µm) column was used with the following conditions: injector, pulsed splitless, 2 µL; carrier gas, helium; column through-flow, 1.0 mL/min; pressure, 12.1 psi; column oven temperature program, 140°C (0.5 min), increase at 5°C/min, 200°C (5 min), increase at 10°C/min, 280°C (10 min), increase at 30°C/min, 300°C (1 min). For each sample three analytical reduplications were performed.

Statistical analysis of the results was conducted using the STATISTICA 7.0 software. Analysis of variance with ANOVA tests was preceded by the Levene's test of homogeneity of variance and the Kolmogorov-Smirnov test of distribution normality (K-S test). Correlation coefficients were calculated, and the significance of differences was examined with the Tukey's test.

RESULTS AND DISCUSSION

Concentrations of PCB congeners in the raw slices of both mackerel and herring (control groups) did not differ significantly ($p \leq 0.05$). Also the process of brining did not affect those con-

TABLE 1. Concentrations of PCB congeners in hot smoked herring slices; data presented as mean±standard deviation.

PCB congeners	Before brining n=5	After brining (3 min) n=25	Smoking duration (h)				
			0.5 n=5	1 n=5	1.5 n=5	2 n=5	2.5 (final product) n=5
Content (ng/g w.w.)							
PCB 28	1.36±0.25	1.33±0.41	1.25±0.15	1.21±0.16	1.28±0.28	1.06±0.14	1.00±0.11
PCB 52	1.79±0.23	1.75±0.12	1.57±0.08	1.50±0.21	1.37±0.34	1.27±0.23	1.22±0.07
PCB 101	6.00±0.87	5.78±0.69	5.27±0.19	5.23±0.41	5.12±0.33	4.44±1.17	4.30±1.25
PCB 118	12.70±0.98	10.59±1.69	10.37±0.48	10.22±0.21	10.17±1.06	9.27±0.82	8.90±0.93
PCB 153	16.50±1.94	15.96±1.88	14.99±1.36	14.09±1.78	14.48±1.63	14.80±1.26	14.01±1.26
PCB 138	12.00±2.84	11.09±1.75	10.03±1.91	10.50±1.63	10.47±1.79	9.91±1.42	9.58±1.47
PCB 180	14.00±1.56	13.61±1.64	12.57±2.01	12.49±0.61	12.08±1.23	12.27±1.23	10.86±1.77
Content (ng/g lipids)							
PCB 28	9.43±1.78	9.42±0.36	8.22±0.84	7.97±1.15	7.18±0.77	5.81±0.50	5.72±1.25
PCB 52	12.41±2.37	12.39±1.57	10.33±0.99	8.65±1.34	7.68±1.54	6.96±1.42	6.77±1.07
PCB 101	41.61±2.47	40.93±3.58	34.67±2.65	30.14±2.11	29.50±1.04	24.34±2.72	23.86±2.18
PCB 118	88.07±2.82	85.00±3.23	68.22±2.19	58.90±2.59	57.04±2.92	50.82±11.66	49.39±2.47
PCB 153	114.42±13.7	99.58±5.61	92.04±4.09	81.21±8.55	83.66±4.65	85.13±3.69	80.32±4.01
PCB 138	83.22±2.44	78.54±2.32	71.09±3.95	67.72±2.91	68.35±2.33	71.95±1.76	70.15±1.96
PCB 180	97.09±2.48	89.31±2.75	82.70±1.49	71.87±3.25	67.75±2.33	69.33±3.98	66.72±2.46

TABLE 2. Concentrations of PCB congeners in hot smoked mackerel slices; data presented as mean±standard deviation.

PCB congeners	Before brining n=5	After brining (3 min) n=25	Smoking duration (h)				
			0.5 n=5	1 n=5	1.5 n=5	2 n=5	2.5 (final product) n=5
Content (ng/g w.w.)							
PCB 28	1.93±0.56	1.90±0.16	1.77±0.27	1.54±0.16	1.37±0.34	1.20±0.19	1.17±0.12
PCB 52	1.32±0.29	1.28±0.11	1.22±0.13	1.19±0.05	0.94±0.18	1.04±0.15	0.96±0.27
PCB 101	2.19±0.14	2.10±0.29	1.92±0.16	1.88±0.17	1.56±0.14	1.58±0.15	1.60±0.19
PCB 118	3.41±0.56	3.24±0.35	3.14±0.24	2.95±0.21	2.68±0.11	2.74±0.17	2.83±0.33
PCB 153	4.10±0.32	3.99±0.64	3.92±0.47	3.90±0.39	3.73±0.24	3.78±0.39	3.82±0.26
PCB 138	4.66±0.72	4.48±1.34	3.76±0.44	3.72±0.42	3.44±0.35	3.50±0.81	3.53±0.41
PCB 180	2.45±0.46	2.40±0.42	2.21±0.13	2.20±0.09	2.23±0.41	2.33±0.60	2.36±0.22
Content (ng/g lipids)							
PCB 28	10.20±0.86	10.26±1.84	9.22±0.46	7.12±0.97	6.08±1.09	5.11±1.36	4.88±0.68
PCB 52	6.97±1.29	6.91±0.55	6.36±0.61	5.50±0.24	4.17±0.39	4.71±0.25	4.01±0.35
PCB 101	11.57±1.28	11.34±1.25	10.01±2.03	8.69±1.28	6.93±1.26	6.73±1.24	6.68±1.46
PCB 118	18.01±1.68	17.49±2.06	16.36±1.17	13.64±2.27	11.90±1.18	11.66±2.13	11.81±1.31
PCB 153	21.66±1.35	21.54±2.41	20.43±1.50	18.03±1.11	16.56±1.65	16.09±1.53	15.86±2.59
PCB 138	24.62±2.40	24.19±1.48	19.59±1.37	17.20±1.76	15.28±1.34	14.81±1.15	14.73±1.39
PCB 180	12.94±1.71	12.96±1.78	11.52±1.11	10.17±0.57	9.90±2.15	9.95±1.17	9.81±1.84

centrations significantly. On the contrary, smoking had a significant effect on PCB content in fish slices (Tables 1, 2, 3). Changes in concentrations of PCB congeners in fish slices were correlated with smoking duration, as well as with PCB concentrations in lipids and with lipid content in tissue (Table 4, Figure 2).

The content of dry matter in the examined raw slices amounted to 36.22±0.62% for hot-smoked mackerel and 36.88±0.21% for cold-smoked mackerel and that of lipids to 18.93± 0.99 and 18.74±0.21%, respectively (Figure 3). The limit of quantification (LOQ) for the examined compounds was 0.1 ng/kg of wet weight on average, which was three times the value of the limit of detection (LOD). The examinations were triplicated, and no significant differences ($p<0.05$) were found between the findings. The recoveries of PCB congeners aver-

TABLE 3. Concentrations of PCB congeners in cold smoked mackerel slices; data presented as mean±standard deviation.

PCB congeners	Before brining n=5	After brining (3 min) n=25	Smoking duration (h)			
			2.0 n=5	4.0 n=5	6.0 n=5	8.0 (final product) n=5
Content (ng/g w.w.)						
PCB 28	1.67±0.12	1.60±0.31	1.79±0.47	1.83±0.27	2.07±015	2.11±0.45
PCB 52	1.36±0.25	1.31±0.18	1.39±0.21	1.47±0.32	1.82±0.37	1.76±0.28
PCB 101	2.10±0.21	1.99±0.29	2.23±0.27	2.27±0.14	3.47±0.49	2.91±0.55
PCB 118	3.31±0.39	3.25±0.14	3.50±0.14	3.80±0.23	4.25±0.24	4.47±0.51
PCB 153	3.52±0.24	3.47±0.19	3.85±0.15	3.97±0.06	4.60±0.22	4.81±0.23
PCB 138	3.49±0.42	3.42±0.13	3.70±0.11	3.93±0.09	4.37±0.25	4.41±0.19
PCB 180	2.77±0.13	2.73±0.07	2.96±0.30	3.22±0.12	3.81±0.14	3.97±0.16
Content (ng/g lipids)						
PCB 28	8.91±1.35	8.60±1.33	9.08±1.41	8.44±0.55	8.94±2.22	8.74±1.48
PCB 52	7.26±0.22	7.04±0.29	7.06±0.78	6.78±0.37	7.86±0.15	7.28±0.78
PCB 101	11.21±1.09	11.21±1.24	11.06±1.30	10.43±1.41	11.67±1.09	11.41±1.96
PCB 118	17.66±1.53	17.47±1.49	17.75±1.51	17.53±2.06	18.37±2.66	18.50±1.45
PCB 153	14.78±0.86	14.68±1.38	15.01±1.45	14.85±0.36	16.46±1.49	16.41±1.73
PCB 138	18.62±1.85	18.39±1.53	18.76±2.03	18.13±1.89	18.88±1.38	18.23±2.56
PCB 180	14.78±1.86	14.69±1.38	15.01±2.45	14.85±3.01	16.46±1.49	16.41±2.73

TABLE 4. Significance ($p<0.05$) of changes in PCB concentrations during hot and cold smoking of mackerel slices and hot smoking of herring slices (Tukey's test).

Cold smoked mackerel (wet weight basis)								Cold smoked mackerel (lipid basis)							
Smoking time	PCB 28	PCB 52	PCB 101	PCB 118	PCB 138	PCB 153	PCB 180	Smoking time	PCB 28	PCB 52	PCB 101	PCB 118	PCB 138	PCB 153	PCB 180
2 h			+	+		+		2 h					+		
4 h			+	+	+	+	+	4 h							
6 h	+	+	+	+	+	+	+	6 h					+		+
8 h	+	+	+	+	+	+	+	8 h							+
Hot smoked mackerel (wet weight basis)								Hot smoked mackerel (lipid basis)							
0.5 h								0.5 h					+		
1.0 h	+							1.0 h	+	+	+		+	+	+
1.5 h	+		+	+	+			1.5 h	+	+	+		+	+	+
2.0 h	+		+	+	+			2.0 h	+	+	+		+	+	+
2.5 h	+		+	+	+			2.5 h	+	+	+		+	+	+
Hot smoked herring (wet weight basis)								Hot smoked herring (lipid basis)							
0.5 h			+					0.5 h	+	+	+	+	+		
1.0 h		+	+					1.0 h	+	+	+	+	+	+	+
1.5 h		+	+					1.5 h	+	+	+	+	+	+	+
2.0 h	+	+	+	+	+		+	2.0 h	+	+	+	+	+	+	+
2.5 h	+	+	+	+	+	+	+	2.5 h	+	+	+	+	+	+	+

+ significant differences,

aged: PCB 28, 77.80±9.18%; PCB 52, 80.47±8.29%; PCB 101, 84.51±1.35%; PCB 118, 86.67±9.76%; PCB 153, 82.82±9.71%; PCB 138, 82.26±9.61; and PCB 180, 88.15±1.71%.

Pesticides Surrogate Spike Mix ranged from 69.9 to 92.8%. Repeatability amounted to 3.26% on average and was assayed by performing 10 quantitative determinations of standard solutions ((N0813; Promochem GmbH, Germany) of seven congeners at a concentration level corresponding to the concentration in the real sample.

Concentrations of the analysed PCB congeners in the raw herring slices (prior to brining) varied from 1.36±0.25 ng/g wet w. to 16.50±1.94 ng/g wet w., while converted to lipid weight

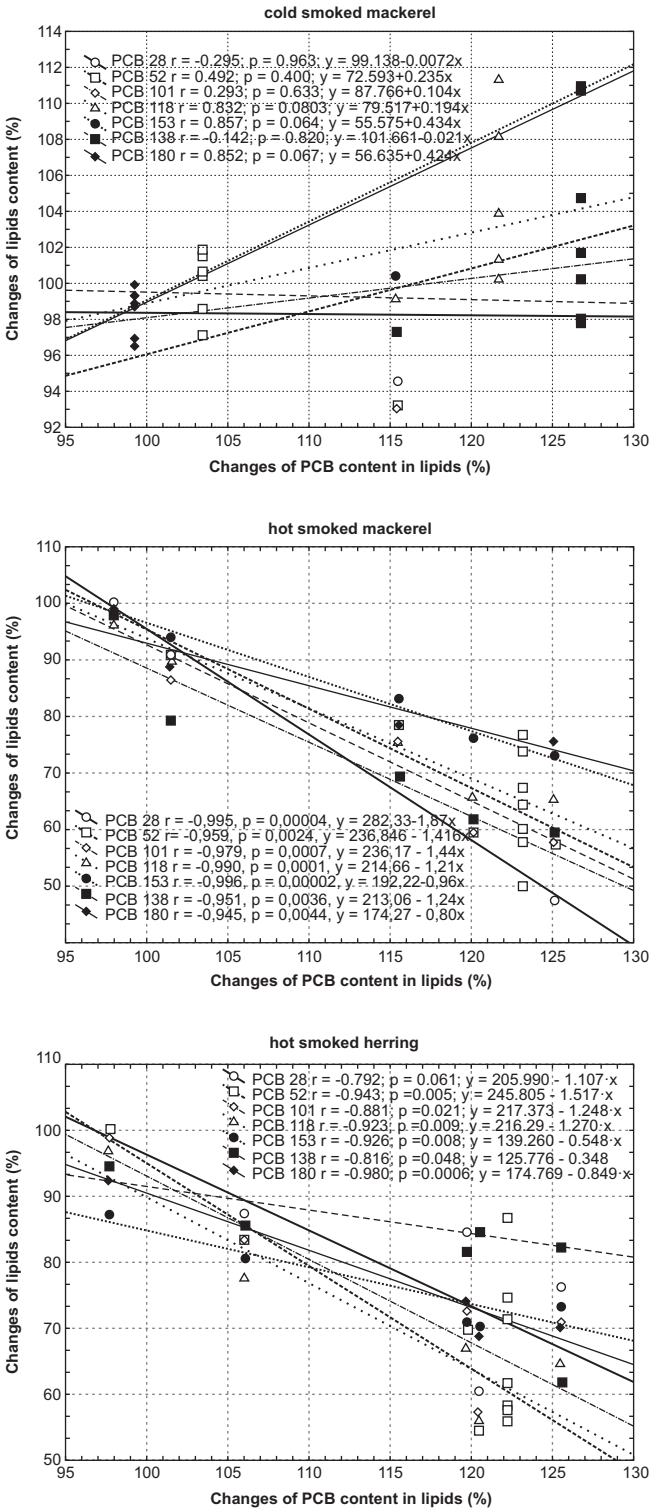


FIGURE 2. Correlations between changes of PCB congeners and lipids in analysed fish slices.

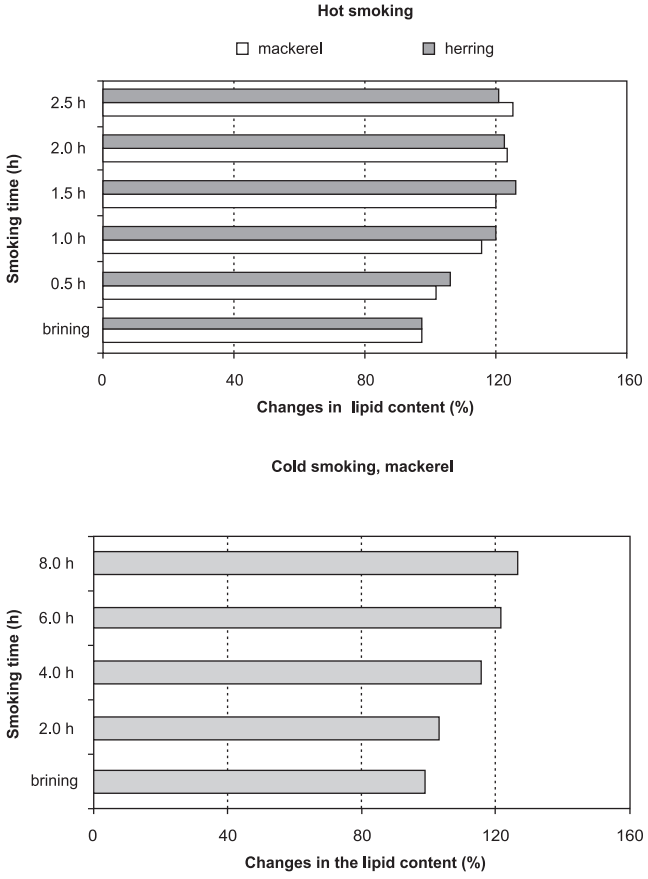


FIGURE 3. Changes in lipid content (%) of fish slices during smoking

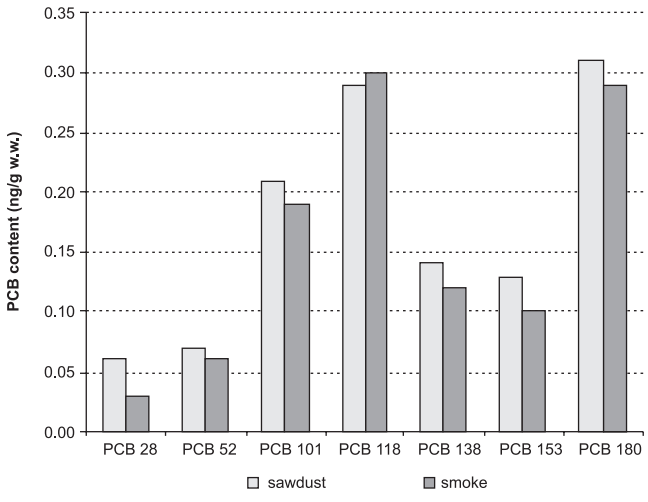


FIGURE 4. PCB residues levels (ng/g w.w.) in the alder sawdust used for smoking and in the generated smoke.

concentrations – from 9.43±1.78 ng/g to 114.42±13.7 ng/g lipids (Table 1). Significant changes in this product were observed as the result of smoking in the contents of all analysed PCB congeners. They depended on smoking duration (Table 1) and also on changes in lipid contents (Figure 2). Hot smoking of herring slices reduced concentrations of the compounds in dry matter in the final product by 15% (PCB 153) to 32% (PCB 52) of the initial level (Table 1). Changes in the concentrations of PCB 101 and PCB 52 were significant during smoking, and those of other compounds after 2 and 2.5 h of the process (Table 4).

In the raw mackerel slices intended for hot smoking, PCB concentrations were slightly lower than in the herring slices and ranged from 1.32±0.29 ng/g w.w. to 4.66±0.72 ng/g w.w. Hot smoking decreased PCB levels in the smoked slices by 3.67% (PCB 180) to 38% (PCB 28) on average. Howev-

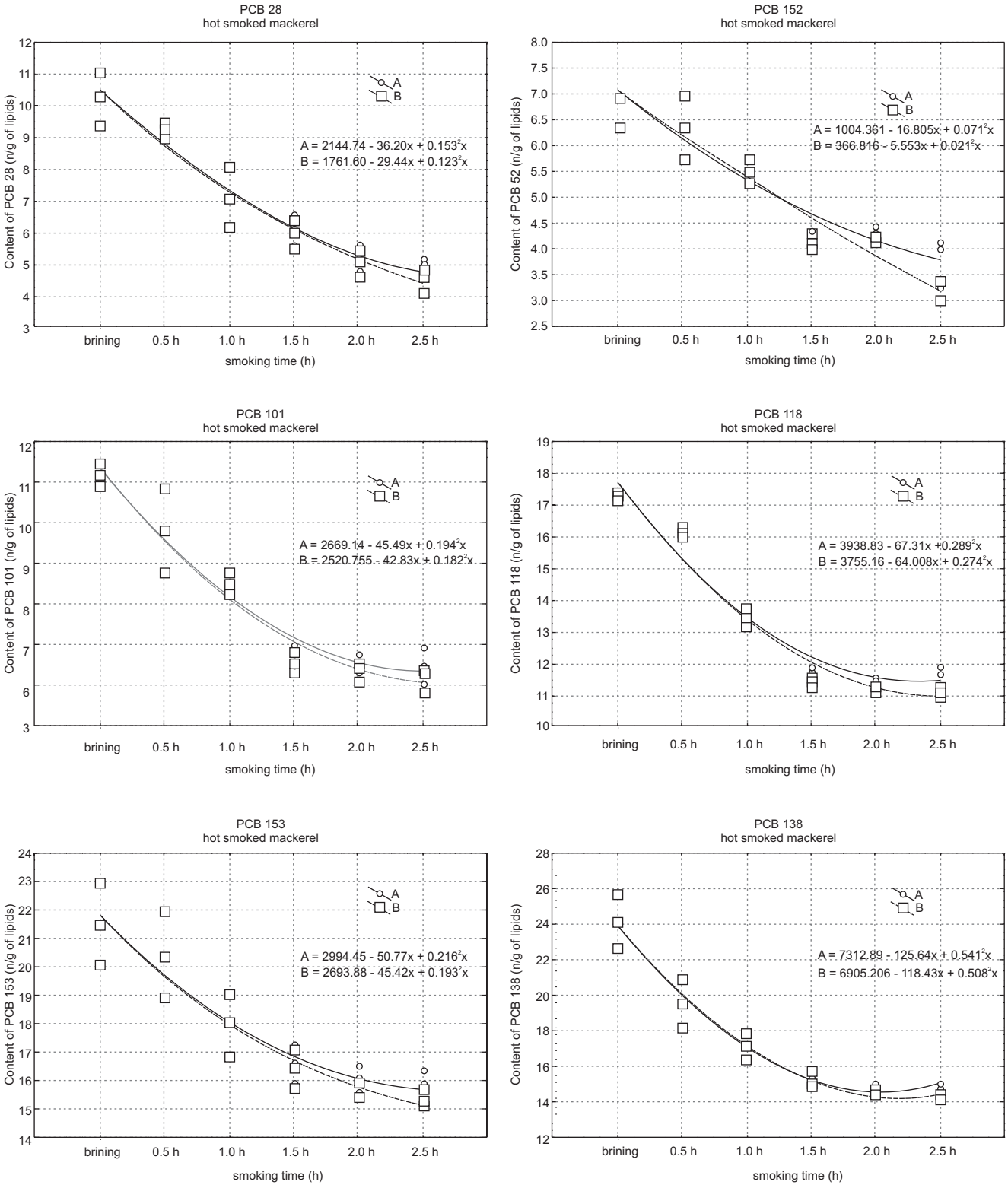


FIGURE 5. The effect of smoke on the PCB concentrations (A-B) in hot smoked mackerel (A – curve of changes in the content of congener in mackerel slices, B – hypothetical curve of changes for PCB congener after subtracting its content in the oil on absorbent paper strips).

er, a slight increase in the levels of five congeners: PCB 180, PCB 118, PCB 153, PCB 138 and PCB 101, was observed during the proper smoking, between the 1.5th and 2.5th h of the process (Table 2). The changes in wet weight were significantly ($p<0.05$) correlated with the smoking duration, especially for PCB 101, PCB 118 and PCB 153 (Table 4).

In the raw mackerel slices intended for cold smoking, PCB concentrations ranged from 1.36±0.25 ng/g w.w. (PCB 52) to 3.52±0.24 ng/g w.w. (PCB 153) (Table 3). During cold smoking (26°C, 8h) PCB content on a wet weight basis increased significantly ($p<0.05$) by 26% (PCB 28, PCB 138) to 43% (PCB 180), while lipid normalized

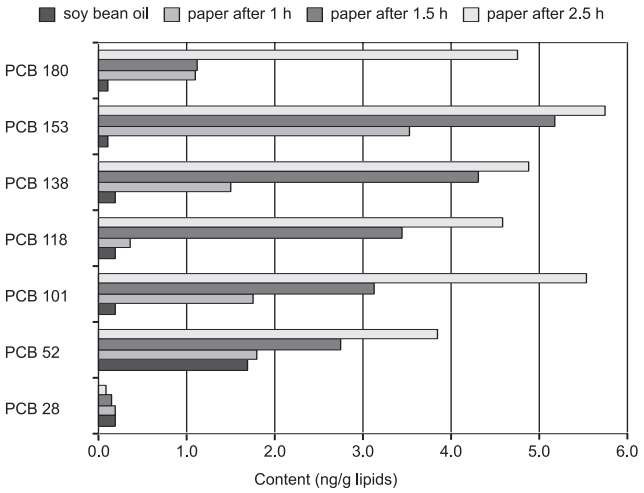


FIGURE 6. Temporal variation of PCB levels (ng/g lipids) in the soybean oil contained in the absorbent paper strips placed in the smoking chamber between the fish slices during hot smoking.

PCB content increased by no more than 11% (PCB 153, PCB 180). In the cold smoked mackerel slices, correlations were observed for concentrations on a lipid weight basis of PCB congeners PCB 118, PCB 153 and PCB 180 (r_{lip} from 0.73 to 0.77) to smoking duration. On a wet weight basis, however, significant ($p<0.05$) relationships to smoking duration were found for all the analysed congeners ($r_{w.w.}$ from 0.75 to 0.94).

During hot smoking of mackerel and herring slices, the PCB 28 congener showed the highest dynamics of losses on both wet weight and lipid weight basis (Table 1, 2). Among the examined congeners, PCB 28 has the highest vapour pressure therefore it easily co-distilled with water vapour during smoking, along with temperature increase from 40 to 80°C.

Figure 2 shows correlation coefficients (r) for relationships between changes in concentrations of PCB congeners and changes in lipid content during smoking. In the hot smoked mackerel slices, strong, negative correlations were found for all congeners ($r_{mackerel}$ from -0.94 to -0.99). In the hot smoked herring slices, such correlations occurred for PCB 153 (r=-0.93), PCB 52 (r=-0.94), PCB 180 (r=-0.98) and PCB 101 (r=-0.88). Changes in the lipid percentage in fish slices, as smoking time increased (hot smoking), did not affect significantly the concentration of PCB congeners in wet tissue, as their losses in the lipid fraction were considerably higher. This is reflected in the strong negative correlations for the changes in the levels of these compounds in lipids during hot smoking of mackerel and herring slices in relation to the changes in the lipids contents (r=-0.792 to r=–0.996) (Figure 2).

This indicates that, despite an increase in lipid content, PCB concentrations decreased due to losses resulting from co-distillation with water vapour during drying (1st h of heat treatment). The slight increases observed in concentrations of PCB 101, 118, 138, 153 and 180 in the final stage of the proper smoking of mackerel slices probably resulted from their presence in the alder sawdust and in the smoke (Figure 4), from which they penetrated into fish slices (Figure 5). This conclusion is supported by the fact that the concentrations of these congeners (except PCB 28) significantly ($p<0.05$) increased after 1.5 and 2.5 h also in the soybean oil on the impregnated paper strips placed among the mackerel slices in the smoking chamber (Figure 6). During cold smoking of mackerel slices, only concentrations of PCB 153, PCB 180 and PCB 118 increased significantly along with the increase in lipid content (r from 0.79 to 0.85), while relationships between changes in concentrations of the other congeners and changes in lipid content had low correlation coefficients – from r=0.03 (PCB 28) to r=0.49 (PCB 52) (Table 5).

Due to high persistence of polychlorinated biphenyls in the temperature range up to 150°C and also due to their resistance to chemical and physical factors [Morita *et al*., 1978; Hansen *et al*.,1999], PCBs could not be thermally degraded during the smoking processes. Dechlorination of *meta* and *para* PCB congeners was reported in temperatures not lower than about 300°C, and less chlorinated congeners were more susceptible to the process [Takasuga *et al*., 1994].

Sherer & Price [1993], in their review study, concluded that cooking processes such as baking, broiling, microwave cooking, poaching, and roasting, removed approximately 20 to 30% of PCBs from fish tissues, while frying appeared to remove more than 50%. They found out that PCB cooking losses were a function of the initial lipid concentration in fish tissue, and were correlated with changes in temperature of heat treatment and with treatment duration.

Also Moya and others [1998] studied the effect of cooking (deep fat frying, pan frying with butter and broiling) on PCB levels in fillets of winter flounder (*Pseudopleuronectes americanus*) with lipid content of 0.8–4.5%. They observed that deep fat frying resulted in a significant reduction in PCBs contents (IUPAC numbers: 8, 18, 28, 44, 52, 66, 101, 105, 118, 128, 138, 153, 180, 187, 195, 206, 209) by 42 to 74%. The deep frying process accelerates the drying of fillets and increases fat content in tissue due to the absorption of the cooking oil. Such a significant reduction of PCB levels may be explained by co-distillation of the compounds with water vapour resulting from the high temperature of frying and by their losses to the cooking oil that acted as an extracting solvent. Poston and others [1996] reported PCB losses in the meat of winter flounder from Bedford Harbour following cooking. Deep fat frying resulted in losses of total PCB content up to 47%, while broiling and pan frying reduced PCB levels by 15–17%. The reduction of total PCB levels corresponded with losses of individual isomers. However, they observed exceptions when levels of some isomers increased following pan frying (PCB 105 and 118) and broiling (PCB 105, 118 and 138). In the earlier work Witczak [2009] showed that thermal treatment significantly influenced changes in PCB residue levels, improving the quality of the examined fish products in terms of organochlorine pollutants content. In the fried fish, percentage losses of the sum of PCBs varied within 32.05% for flounder and 81.11% for cod. Also Ciereszko & Witczak [2003], in their study on losses of *non*-ortho and *mono*-ortho PCB congeners following cooking, observed that the highest average losses resulted from deep fat frying (57%), and the lowest ones – from roasting in a microwave oven (13%). According to Salama and others [1998], various cooking methods re-

duced PCB levels in Atlantic bluefish (*Pomatomus saltatrix*) fillets as follows: smoking – 65%, microwave baking – 60%, charbroiling with skin off – 46%, charbroiling with skin on – 37%, pan frying – 27%, and convection oven baking – 39%.

To date, not much attention has been focused on changes in PCB content during the process of fish smoking. However, both hot and cold smoking are important methods of fish processing in the Polish food industry, and smoked fish are in demand on the market.

CONCLUSIONS

Concluding the above, hot smoking reduced levels of indicatory PCB congeners (IUPAC numbers 28, 52, 101, 118, 138, 153, 180) in herring slices by 15–32%, while in mackerel slices – by 3.7–38%. In contrast, cold smoking resulted in an increase of PCB levels by 26–43%. During the drying of fish slices, PCBs may co-distil with water vapour and settle on the walls of the smoking chamber and smoking trolleys. During the next stage of the smoking process, the proper smoking, they can be released with the smoke back to the smoking chamber and settle on the surface of the smoked fish together with the disperse phase of the smoke (aerosol). This thesis was confirmed by the analysis of saw dust used for smoking and by the experiment with the absorbent paper strips soaked in soybean oil and placed in the smoking chamber between the fish slices (Figure 4, 5).

It should also be remembered that the smoking chamber is used in a constant mode, so PCBs settled with the smoke aerosol on the chamber walls, chimney flues and smoking trolleys during the smoking of one batch of fish, may be released back during the smoking of next batches and be absorbed by the smoked products.

The fish examined in this study were harvested from a relatively clean environment of the Norwegian Sea, which is much less polluted by harmful chemicals, including organochlorine dioxin-like PCBs, than the Baltic Sea. Studies of Atuma and others [1998] and Falandysz and others [2002] revealed that herring fish harvested from the Baltic Sea had considerably higher levels of the examined PCB congeners. Therefore, the problem of PCB intake from marine food products is still a topical issue and requires constant monitoring.

Comparing the contents of indicatory PCB congeners in fish slices after hot and cold smoking and earlier presented data for dioxin-like PCBs [Hansen *et al*., 1999], similar correlations were concluded. The results obtained suggested that cold smoked fish pose increased health risk, therefore should be consumed rather rarely.

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