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Effect of Smoking Process on Changes in the Content of Selected Non-*ortho*- and Mono-*ortho*-PCB Congeners in Mackerel Slices

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The study involved determination of changes in the content of toxic dioxin-like coplanar non-*ortho* (PCB 77, PCB 126, PCB 169) and mono-*ortho* (PCB 156, PCB 157, PCB 114) congeners in mackerel slices during cold and hot smoking. In addition, the risk of toxicological exposure of the consumers of examined smoking products was assessed by calculating toxic equivalency (TEQs) in relation to 2,3,7,8-TCDD dioxin. In the final stages of hot smoking a small increase was observed in the content of analyzed compounds due to the presence of PCBs in the smoke. The main factor determining the changes in the content of these compounds in fish slices may have been their loss with the lipid leakage and in codistillation with water vapor. The hot smoking of mackerel slices contributed to a decrease in the content of examined non-*ortho*- and mono-*ortho*-PCB congeners in final products and in consequence to a drop of TEQs by 14.2%. On the other hand, cold smoking led to a rise in the content of analyzed PCB congeners in the final product, which significantly affected the increase of TEQs level by 31.7% in relation to initial raw material.

KEYWORDS: Non-*ortho*- and mono-*ortho*-polychlorinated biphenyl (PCB) congeners; mackerel; smoking

INTRODUCTION

Industrial and municipal effluents as well as solid wastes disposed on dump sites, from which they can escape into the atmosphere and penetrate into the soil and surface waters, are commonly considered to be the main sources of aquatic environment polychlorinated biphenyl (PCB) pollution (*1*, *2*). These compounds—as lipophiles—with exceptionally high stability in the natural environment accumulate in all trophic chain links, that is, from phytoplankton to fishes in aquatic reservoirs. Highest PCB concentrations in aquatic organisms are recorded at the peak of top of the food chain, namely, in predatory fishes and sea mammals and, as a consequence, in the consumers of marine food products (*3*, *4*).

The presence of stable toxic compounds may constitute a hazard for consumer health. As fish are mostly eaten in the form of processed products, an important issue is thus to identify the effect of technological processes and culinary treatments on changes in these compounds in final products.

In the available literature a lot of attention is devoted to examinations that concern changes in total PCB content during thermal processing of some fish species (*5*−*15*). These works referred mostly to cooking, frying, traditional roasting, and heat treatment in microwave ovens as well as grilling. On the other hand, few papers were devoted to changes in PCB content in fishes during the smoking process (*10*, *14*).

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In Poland, the smoked fish industry is an important branch in fish processing, delivering to the market products that are in great demand.

Due to the fact that specific PCB congeners are characterized by different toxicities (*16*, *17*), in particular the coplanar congeners are toxic for living organisms, being antiestrogenic and neurotoxic as well as probably carcinogenic. These congeners are three-dimensional analogues of 2,3,7,8-TCDD dioxin and are similar to it in their biological activity (*18*).

The present study aimed at determining the effect of hot and cold smoking on changes in the content of toxic non-*ortho* (PCB 77, PCB 126, PCB 169) and mono-*ortho* (PCB 156, PCB 157, PCB 114) congeners in mackerel slices. Also, the risk of toxicological exposure of the consumers of the examined smoking products was assessed by calculating dioxin toxic equivalents (TEQs).

MATERIALS AND METHODS

Sampling. The material for analyses consisted of double mackerel slices (double fish flaps) (according to the Polish Norm PN-A-86770) from fish caught in the Norwegian Sea in September 2001 that were delivered as whole frozen fish. After defrosting, these slices were cut along the dorsal line into two equal parts and exposed to smoking after brining according to the diagram (**Figure 1**).

Smoking was carried out under industrial conditions in an "Atmos"-type smoking chamber (**Figure 2**). This chamber was equipped with automatic temperature and humidity control and had a forced air circulation heating system. The smoke was supplied from a smoke

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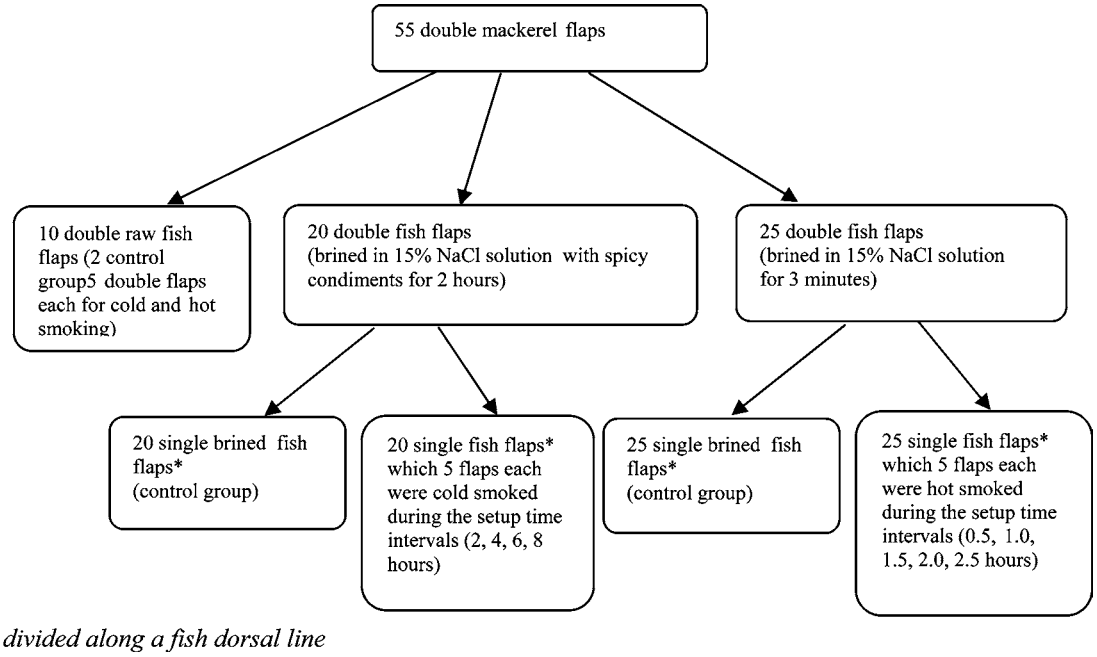

Figure 1. Scheme of the experiment.

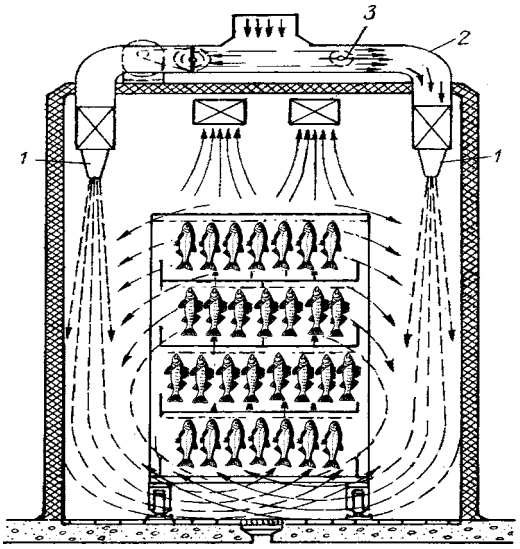

Figure 2. Schematic diagram of the "Atmos" smoke chamber (*19*): 1, hot air and smoke nozzles; 2, smoke return passages; 3, gate valve for alternate free passage of smoke into the smoking chamber.

generator situated outside the smoke chamber. This setup enabled uniform smoking of raw material within the whole chamber.

Before smoking, mackerel slices were brined in 15% NaCl aqueous solution for 3 min before hot smoking and for 3 h before cold smoking (the latter together with the spice condiments laurel leaves, allspice, paprika, and mustard). To determine changes during brining, five slices were split longitudinally into single slices, of which some were the control and others were brined as a whole.

Two kinds of smoking were used.

Hot Smoking. After brining, 5five double slices were sampled randomly and cut into respective portions assigned for smoking during the set time intervals.

In the first hour of smoking, the slices partly dried at 40 °C. Thereafter, proper hot smoking was initiated by supplying the smoke into the smoke chamber and raising the temperature gradually to 80 °C. The hot-smoking process lasted for 2.5 h.

In addition, 28 × 7 cm absorbent paper strips soaked in soybean oil, that is, of average single mackerel slice surface (196 cm^2), were hung on the upper smoking bars.

The smoke chamber charge contained two smoking trolleys, storing in total ≈120 kg of raw material. Alder sawdust consumption amounted to 20 kg/smoking cycle.

Cold Smoking. The samples of mackerel slices for cold smoking were prepared similarly. Fish slices for analyses were sampled from the smoking chamber after 2, 4, and 6 h of smoking as well as the final products after 8 h. The smoking was carried out at 27 °C. The smoking chamber contained two smoking trolleys, storing in total ≈160 kg of raw material. The alder sawdust consumption was ≈40 kg/smoking cycle.

Analytical Methods and Instrumentation. To determine weight losses, the slices were weighed before and after the brining and the smoking. The samples collected from the smoking chamber were packed into polyethylene bags and frozen at −18 °C until analysis. For all samples, dry matter and lipid contents were determined.

To determine which PCB congeners pass from the sawdust into the smoke, destructive alder sawdust distillation directly to *n*-hexane was performed under laboratory conditions after the cooler had been rinsed every time with *n*-hexane and the rinsate had been added to the sample.

For PCB analysis, the slices were deskinned, minced, and homogenized, sampling thereafter three times 30 g weighed amounts each of wet muscle tissue (three replications).

All samples were fortified with 50 μL of Pesticides Surrogate Spike Mix (Supelco), being a solution of decachlorobiphenyl and 2,4,5,6-tetrachloro-*m*-xylene dissolved in acetone. Part of the samples was fortified with a known amount of single PCB congeners to identify the examined compounds correctly and to determine recovery. As a substitute reference material, a "chlorobiphenyls in mackerel oil" no. 350 (Promochem GmbH, Wesel, Germany), which included seven indicatory congeners (PCB 28, 52, 101, 118, 138, 153, 180) was used. For the analysis, a standard solution of six congeners dissolved in isooctane (Promochem GmbH,) and single standards of these compounds were used. The samples were dried and comminuted in mortar with anhydrous Na_2SO_4 (roasted at 400 °C for 4 h) until uniform dry matter had been obtained (according to PN-EN 1528-2). To extract the PCBs together with lipids, a 50 cm^3 acetone/*n*-hexane solution (v/v) (2.5:1) was used each time, followed by a 50 cm^3 *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 cm^3 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

Table 1. Contents of Non-*ortho*-PCB Congeners in Hot-Smoked Mackerel Slices in Terms of Wet Weight and Lipid Weight

non-*ortho* congener	before brining, $n = 5$	after brining (3 min), $n = 25$	smoking time: 0.5 h, $n = 5$	1 h, $n = 5$	1.5 h, $n = 5$	2 h, $n = 5$	2.5 h (final product), $n = 5$
			Contents (ng·kg^{-1} of Wet Weight)				
PCB 77	1.92 ± 0.40	1.81± 0.20	1.78 ± 0.19	1.66 ± 0.31	1.47 ± 0.31	1.41 ± 0.21	1.36 ± 0.19
PCB 126	2.47 ± 0.19	2.40 ± 0.16	2.19 ± 0.06	1.94 ± 0.19	1.98 ± 0.15	2.01 ± 0.23	2.04 ± 0.21
PCB 169	1.94 ± 0.09	1.81 ± 0.14	1.70 ± 0.08	1.46 ± 0.12	1.49 ± 0.08	1.58 ± 0.11	1.63 ± 0.21
			Contents (ng·kg^{-1} of Lipids)				
PCB 77	10.1 ± 0.21	9.72 ± 0.21	9.28 ± 0.07	7.67 ± 0.05	6.53 ± 0.11	6.00 ± 0.51	5.64 ± 0.45
PCB 126	13.1 ± 0.03	13.0 ± 0.07	11.4 ± 0.07	8.97 ± 0.02	8.79 ± 0.11	7.56 ± 1.76	7.51 ± 1.64
PCB 169	10.3 ± 0.51	9.77 ± 0.37	8.96 ± 0.38	6.75 ± 0.62	6.62 ± 0.38	6.73 ± 0.24	6.80 ± 0.35

Table 2. Concentrations of Non-*ortho*-PCB Congeners in Cold-Smoked Mackerel Slices in Terms of Wet Weight and Lipid Weight

non-*ortho* congener	before brining, $n = 5$	after brining (3 h), $n = 20$	smoking time: 2.0 h $n = 5$	4.0 h $n = 5$	6.0 h $n = 5$	8.0 h (final product), $n = 5$
			Contents (ng·kg^{-1} of Wet Weight)			
PCB 77	2.26 ± 0.06	2.19 ± 0.17	2.27 ± 0.22	2.33 ± 0.23	2.62 ± 0.08	2.85 ± 0.06
PCB 126	2.21 ± 0.14	2.17 ± 0.19	2.29 ± 0.01	2.27 ± 0.15	2.61 ± 0.23	2.90 ± 0.19
PCB 169	1.87 ± 0.08	1.81 ± 0.15	2.00 ± 0.14	2.14 ± 0.15	2.53 ± 0.16	2.56 ± 0.15
			Contents (ng·kg^{-1} of Lipids)			
PCB 77	12.1 ± 1.01	11.8 ± 0.31	11.5 ± 0.46	10.8 ± 0.48	11.4 ± 0.38	11.8 ± 0.31
PCB 126	11.8 ± 0.29	11.7 ± 0.42	11.6 ± 0.47	10.5 ± 0.21	11.3 ± 0.69	12.0 ± 0.25
PCB 169	9.98 ± 0.14	9.73 ± 0.35	10.1 ± 1.01	9.87 ± 0.48	10.9 ± 0.86	10.6 ± 0.67

Table 3. Concentrations of Mono-*ortho*-PCB Congeners in Hot-Smoked Mackerel Slices in Terms of Wet Weight and Lipid Weight

mono-*ortho* congener	before brining, $n = 5$	after brining (3 min), $n = 25$	smoking time: 0.5 h, $n = 5$	1 h, $n = 5$	1.5 h, $n = 5$	2 h, n = 5	2.5 h (final product), $n = 5$
			Contents (ng·kg^{-1} of Wet Weight)				
PCB 114	2.26 ± 0.29	2.02 ± 0.32	2.01 ± 0.11	1.77 ± 0.29	1.55 ± 0.29	1.35 ± 0.21	1.26 ± 0.19
PCB 156	2.53 ± 0.11	2.28 ± 0.21	1.96 ± 0.16	1.68 ± 0.11	1.86 ± 0.21	1.99 ± 0.14	2.05 ± 0.04
PCB 157	1.48 ± 0.29	1.40 ± 0.16	1.28 ± 0.09	1.21 ± 0.20	1.21 ± 0.19	1.25 ± 0.08	1.27 ± 0.13
			Contents (ng·kg^{-1} of Lipids)				
PCB 114	11.9 ± 0.04	10.9 ± 0.44	10.8 ± 0.11	8.18 ± 0.59	6.88 ± 0.09	5.75 ± 0.11	5.26 ± 0.19
PCB 156	13.4 ± 0.11	12.4 ± 0.11	10.2 ± 0.30	7.77 ± 0.19	8.24 ± 0.24	8.47 ± 0.51	8.56 ± 0.33
PCB 157	7.82 ± 0.39	7.56 ± 0.11	6.67 ± 0.31	6.13 ± 0.29	5.62 ± 0.41	5.32 ± 0.29	5.30 ± 0.77

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 cm^3. The samples were purified by adding 6 cm^3 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 cm^3 LiChrolut columns on an anhydrous Na_2SO_4 bed. The samples were concentrated in a vacuum rotary evaporator to 0.1 cm^3 and placed in the glass insert (0.2 cm^3) of screw-cap vials (1 cm^3), storing them 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^{-1}; 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 testing included analysis of variance (ANOVA) (Statistica 6.1 software package), calculation of correlation coefficients, and linear regression equations.

RESULTS AND DISCUSSION

Brining of mackerel slices preceding the two smoking processes did not affect the changes in the levels of analyzed compounds ($p < 0.05$) (**Tables 1**−**5**).

Table 4. Coefficients of Correlation (*r*) between the Changes in the Contents of Analyzed Congeners (Percent) and the Changes in the Lipid Levels (Percent) ($p < 0.5$)

PCB congener	hot-smoked mackerel: *r* in wet weight	hot-smoked mackerel: *r* in lipids	cold-smoked mackerel: *r* in wet weight	cold-smoked mackerel: *r* in lipids
PCB 77	–0.873	–0.972	0.915	0.694
PCB 126	–0.700	–0.939	0.969	0.819
PCB 169	–0.678	–0.968	0.981	0.879
PCB 114	–0.884	–0.980	0.954	0.309
PCB 156	–0.578	–0.862	0.945	0.280
PCB 157	0.074	–0.675	0.956	0.905

The content of dry weight 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.

The limit of quantification (LOQ) for the examined compounds was 0.02 ng·kg^{-1} 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 averaged PCB 77, 61.35 ± 7.55%; PCB 126, 69.55 ± 3.79%; PCB 169, 77.60 ± 1.27%; PCB 114, 78 ± 2.85%; PCB 156, 79 ± 3.01%; and PCB 157, 82.57 ± 2.15%.

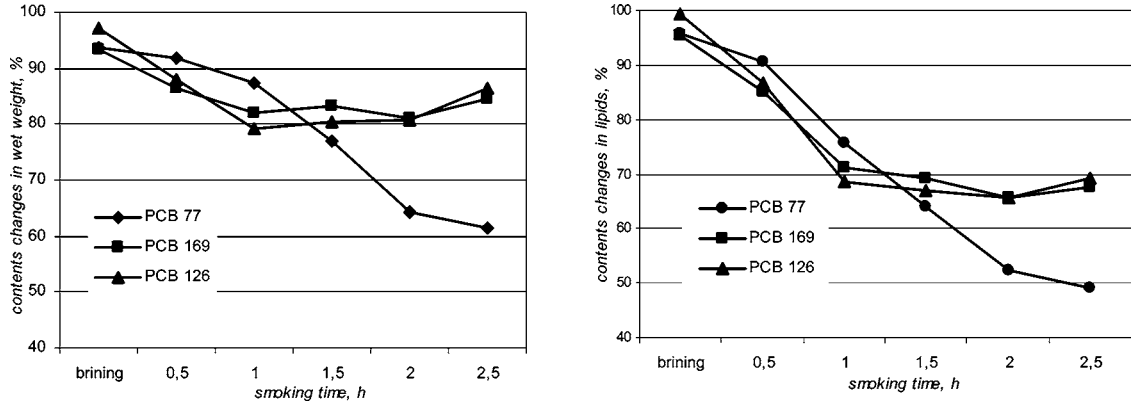

Figure 3. Percentage changes of non-*ortho*-PCB congeners in hot-smoked mackerel slices with smoking time length.

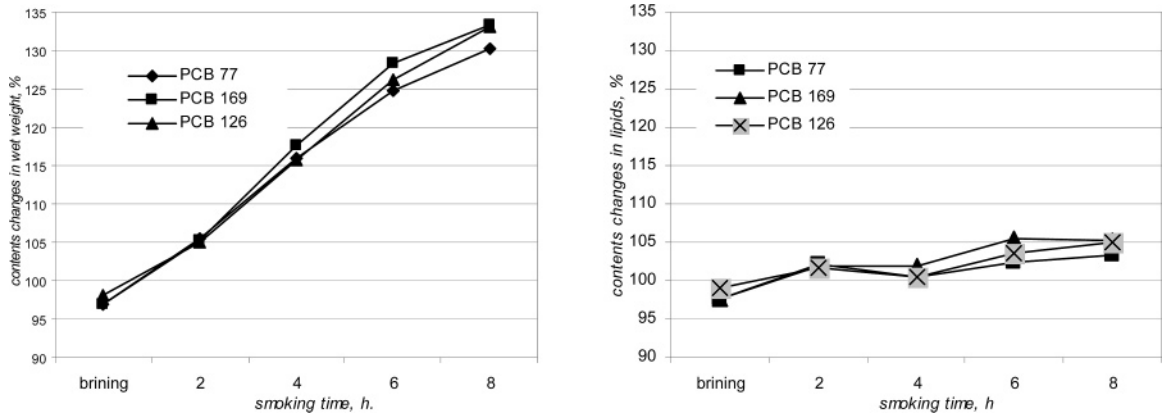

Figure 4. Percentage changes of non-*ortho*-PCB congeners in cold-smoked mackerel slices with smoking time length.

Table 5. Concentrations of Mono-*ortho*-PCB Congeners in Cold-Smoked Mackerel Slices in Terms of Wet Weight and Lipid Weight

			smoking time			
mono-*ortho* congener	before brining, $n = 5$	after brining (3 h), $n = 20$	2.0 h, $n = 5$	4.0 h, $n = 5$	6.0 h, $n = 5$	8.0 h (final product), $n = 5$
			Contents (ng·kg^{-1} of Wet Weight)			
PCB 114	2.40 ± 0.16	2.36 ± 0.11	2.45 ± 0.06	2.38 ± 0.07	2.64 ± 0.18	2.98 ± 0.08
PCB 156	2.51 ± 0.21	2.41 ± 0.08	2.63 ± 0.07	2.86 ± 0.05	3.02 ± 0.19	3.29 ± 0.08
PCB 157	1.51 ± 0.13	1.47 ± 0.05	1.70 ± 0.09	1.79 ± 0.07	2.19 ± 0.07	2.39 ± 0.08
			Contents (ng·kg^{-1} of Lipids)			
PCB 114	12.8 ± 0.43	12.7 ± 0.47	12.4 ± 1.59	11.0 ± 0.59	11.4 ± 1.24	12.3 ± 0.75
PCB 156	13.3 ± 0.69	12.9 ± 0.90	13.3 ± 0.64	13.2 ± 0.55	13.1 ± 0.44	13.6 ± 0.39
PCB 157	8.06 ± 0.90	7.90 ± 0.31	8.62 ± 0.34	8.21 ± 0.81	9.46 ± 0.49	9.88 ± 0.18

The obtained recovery of Pesticides Surrogate Spike Mix ranged from 69 to 88%. Repeatability amounted to 1.35% on average and was determined by performing 10 quantitative determinations of six congener standard solutions (Promochem GmbH) on concentration level corresponding to the concentration in real sample.

Significant changes were observed as the result of smoking in the contents of all analyzed non-*ortho*-PCBs. They depended on smoking time lengths (**Table 1**; **Figures 3** and **4**) and also on changes in the percentage of lipid contents (**Figure 5**).

During hot smoking of mackerel slices, the greatest loss (up to 38.5% in dry matter in the final product) was observed for PCB 77 (**Figure 3**). This compound, of lowest chlorine level in relation to the other congeners, is characterized by the highest vapor pressures; thus, it volatilizes more easily in codistillation with water vapor (*20*).

A significant increase ($r = 0.875$) of PCB 77 occurred as the result of cold smoking, by some 30.7% in the final product (**Table 3**; **Figure 4**). According to Sherer and Price (*12*), the temperature of thermal processing determines significantly the rate of volatilization.

During hot smoking, losses were also found in the contents of PCB 126 and PCB 169 (13.6 and 15.5%, respectively), with the maximal decrease starting after 1 h of partial drying (12−13%) and followed by small changes after 1.5 and 2 h of smoking; there was a consistent increase in the final product after 2.5 h.

For cold smoking, a statistically significant increase of PCB 126 content in the mackerel slices ($p < 0.05$; $r_{ww} = 0.918$, $r_{lipid} = 0.819$) was observed at 8 h, both in the wet weight (33.3%) and the lipids (5.0%) (**Table 2**; **Figure 4**). The changes in the content of PCB 169 congener were similar to those for PCB 126.

When the contents of mono-*ortho*-PCB congeners in hot-smoked mackerel slices were analyzed, a strong correlation ($r_{ww} = -0.905$, $r_{lipid} = -0.972$) was found only for the losses of PCB 114 in relation to the length of smoking time (**Table 3**; **Figure 6**).

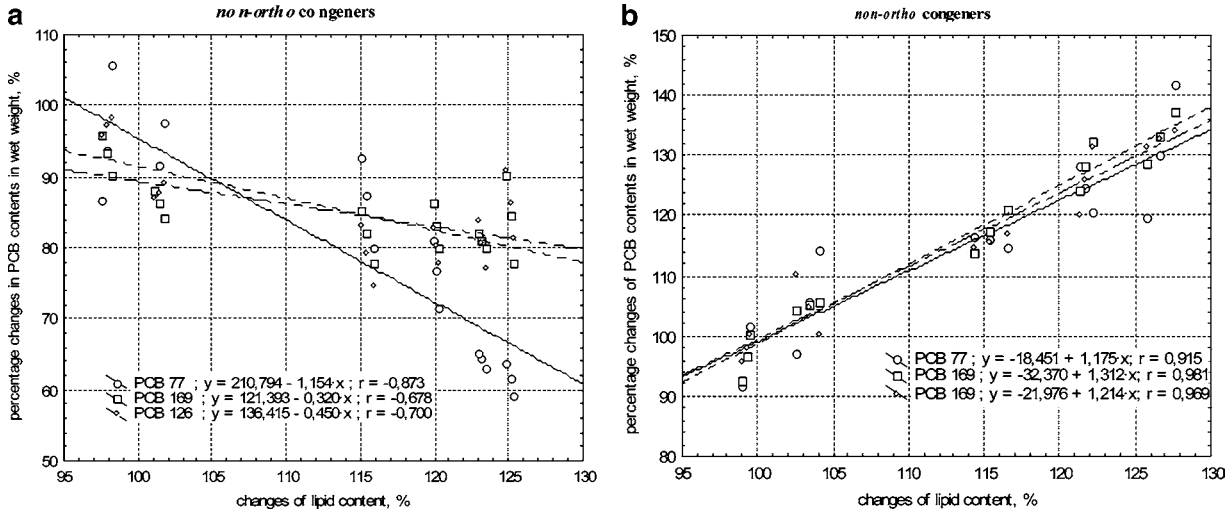

Figure 5. Correlations between percentage changes of non-ortho-PCB congeners and lipids in hot-smoked (**a**) and in cold-smoked mackerel (**b**) ($p < 0.05$).

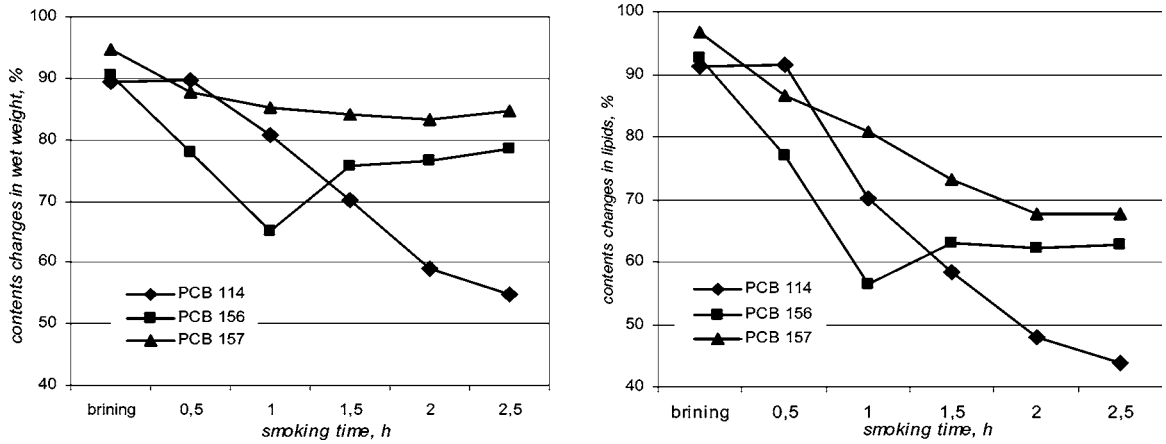

Figure 6. Percentage changes in the content of mono-*ortho*-PCB congeners in hot-smoked mackerel slices with smoking time length.

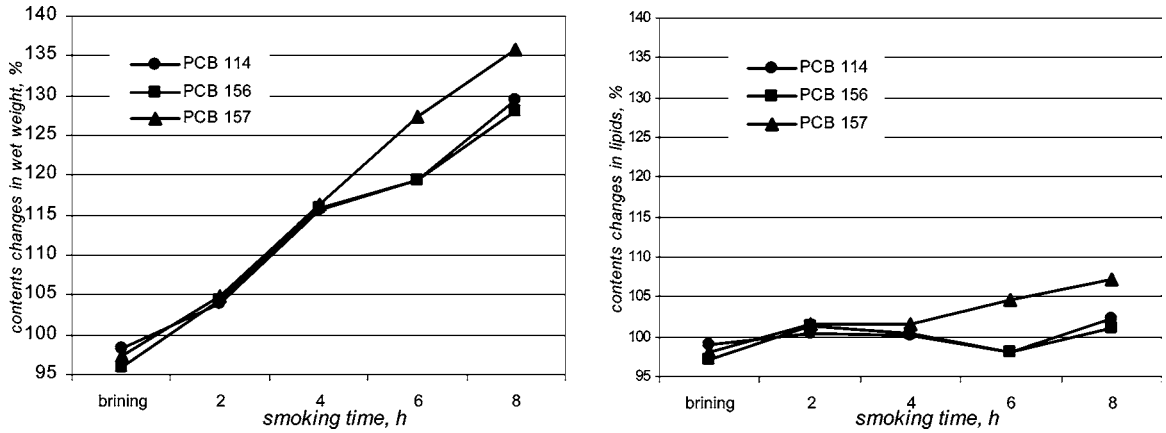

Figure 7. Percentage changes in the concentrations of mono-*ortho*-PCB congeners in cold-smoked mackerel slices with smoking time length.

Changes in the lipid percentage in the examined fish slices, as smoking time increased, did not affect significantly the concentration of PCBs 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 congeners in lipids during hot smoking of mackerel slices in relation to the changes in the lipid contents ($r = -0.578$ to -0.980) (**Table 4**).

On the other hand, cold smoking affected significantly ($p < 0.05$; $r = 0.907-0.936$) the dynamics of content increases for PCB 114, PCB 156, and PCB 157 (**Table 5**; **Figure 7**).

During cold smoking, as the lipid content increased in the mackerel slices, a very strong positive correlation was found only for PCB 157 ($r = 0.914$, $p < 0.05$), whereas the changes in the levels of PCB 114 and PCB 156 were characterized by low correlation coefficients: $r = 0.311$ and $r = 0.280$ ($p < 0.05$), respectively.

Positive correlations between the contents of the examined congeners in wet tissue and the changes in the lipid fraction during cold smoking testify to smaller losses of these compounds in codistillation with water vapor due to a basically lower temperature in the smoking chamber and a more compact

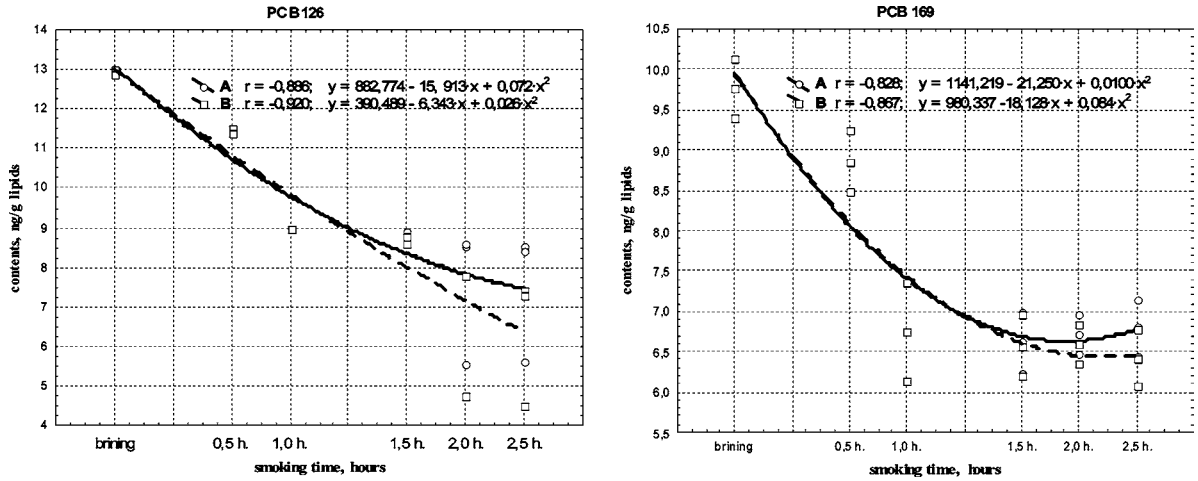

Figure 8. Effect of smoke on the content of PCB 126 and PCB 169 (**A**, **B**) in hot-smoked mackerel (**A**, changes in the content of congener in mackerel slices; **B**, hypothetical curve of changes for PCB congener after subtracting its content in the oil on impregnated paper strips).

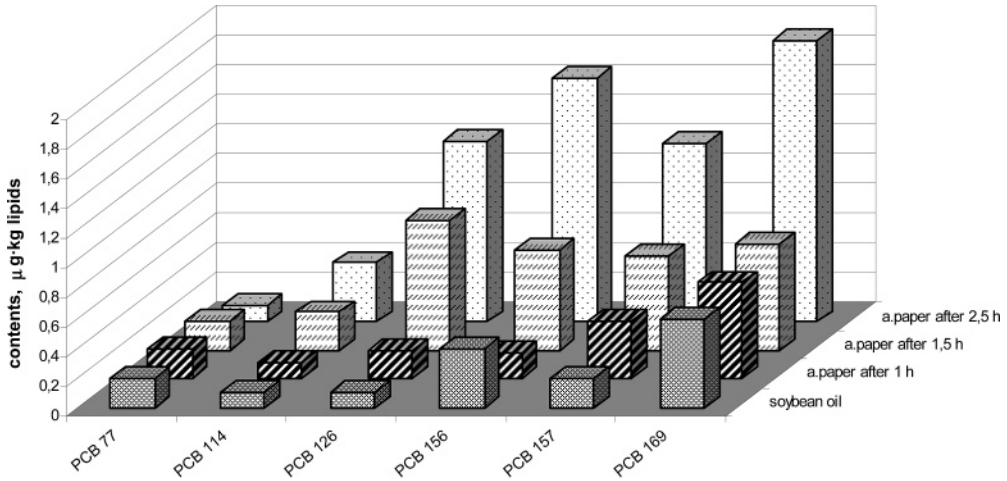

Figure 9. Contents of analyzed PCB congeners in the soybean oil contained in impregnated paper (a.paper) placed in the smoking chamber together with fish charge during hot smoking with time.

structure of the muscle tissue in comparison with hot-smoking tissue (**Table 4**). The speed of physical vapor deposition (PVD) and chemical vapor deposition (CVD) of smoke compounds on moist surfaces is higher than that on dry surfaces (*21*). Cold smoking was not preceded by predrying, as in case of hot smoking (1 h at 40 °C), but the exposure of fish slices to smoke started directly after they had been removed from the brine and hung on smoking trolleys.

Statistical analysis of changes in the contents of coplanar PCB congeners in the mackerel slices during hot smoking showed different negative correlations in wet tissue and in lipids (**Table 4**). Thus, as a result, despite the increase in the lipid content in the smoked fish, a decrease took place in the concentration of PCBs. This testifies to their loss in codistillation with water vapor during partial drying, and a small increase of their content in the final stages of smoking, in particular of PCB 169 and PCB 126 (**Figure 3**), was probably caused by their presence in the smoke aerosol and their penetration into fish slices (**Figure 8**).

This is proved by the increase of the content of these congeners in the oil on impregnated paper strips hung in the smoking chamber (**Figure 9**), which may be estimated at 13.3% for PCB 126 and at 5.8% for PCB 169 in the final product.

The coplanar congeners in soybean oil on impregnated paper strips rose during smoking, with significant increases ($p < 0.05$) in the contents of other analyzed coplanar congeners (except for PCB 169) after 1.5 and 2.5 h (**Figure 9**). The exception was PCB 77 (**Figure 9**), for which no increase was found but which did show a significant drop after 2.5 h of smoking.

On the other hand, analysis of the alder sawdust used for smoking and the smoke obtained from it during destructive wood distillation showed all analyzed congeners (**Figure 10**) except for PCB 77.

The high stabilities of polychlorinated biphenyls and their chemical and physical resistance exclude their thermal degradation at assumed temperatures during smoking.

Similar conclusions were obtained by Zabik et al. (*10*), Salama et al. (*14*), and Ciereszko and Witczak (*15*) in their studies; these authors examined many methods of thermal processing with respect to different fish species.

To determine the health risk connected with the consumption of examined smoked products, toxic equivalency (TEQ) was calculated for each of them (**Tables 6** and **7**) from the relationship

$$\mathrm{TEQ} = \Sigma[\mathrm{PCB}_i]\mathrm{TEF}_i$$

where PCB_i is the concentration of the *i*th congener ($\mathrm{ng \cdot kg^{-1}}$) and TEF_i is the toxic equivalents factor of the *i*th congener calculated in relation to 2,3,7,8-TCDD dioxin (*18*, *22*).

In the final products, TEQs were mainly a derivative of changes in the contents of PCB 126 and PCB 169, with toxic

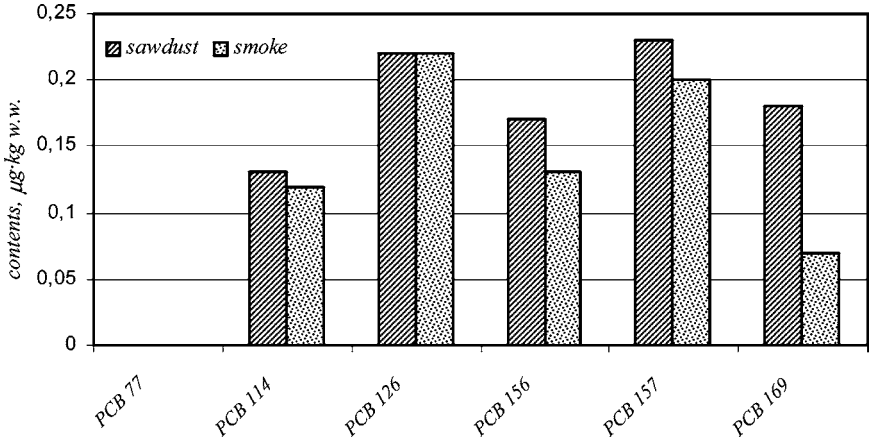

Figure 10. Contents of analyzed PCB congeners in the alder sawdust used for smoking and the generated smoke.

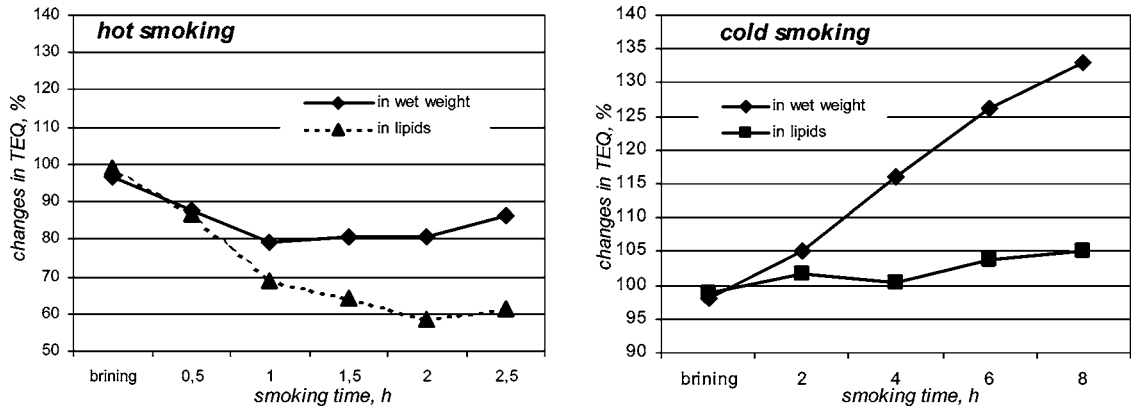

Figure 11. Percentage changes in toxic equivalency (TEQs) during hot and cold smoking of mackerel slices relative to raw tissue.

Table 6. Toxic Equivalency (TEQs) in Cold-Smoked Mackerel Relative to Raw Tissue before (A) and after (B) Processing

smoking time (h)	*n*	contents (ng-TEQ·kg^{-1} of wet weight) TEQs (A)	TEQs (B)	contents (ng-TEQ·kg^{-1} of lipids) TEQs (A)	TEQs (B)
brining	5	0.24 ± 0.02	0.24 ± 0.02	1.30 ± 0.03	1.28 ± 0.05
2	5	0.24 ± 0.01	0.25 ± 0.00	1.26 ± 0.12	1.28 ± 0,06
4	5	0.22 ± 0.01	0.25 ± 0.02	1.16 ± 0.09	1.16 ± 0.03
6	5	0.23 ± 0.01	0.29 ± 0.03	1.21 ± 0.12	1.25 ± 0,08
8	5	0.24 ± 0.01	0.32 ± 0.02	1.26 ± 0.06	1.32 ± 0.03

Table 7. Toxic Equivalency (TEQs) in Hot-Smoked Mackerel Relative to Raw Tissue before (A) and after (B) Processing

smoking time (h)	*n*	contents (ng-TEQ·kg^{-1} of wet weight) TEQs (A)	TEQs (B)	contents (ng-TEQ·kg^{-1} of lipids) TEQs (A)	TEQs (B)
brining	5	0.27 ± 0.02	0.26 ± 0.02	1.43 ± 0.00	1.41 ± 0.01
0.5	5	0.27 ± 0.01	0.24 ± 0.01	1.45 ± 0.02	1.25 ± 0.01
1.0	5	0.27 ± 0.01	0.21 ± 0.02	1.42 ± 0.02	0.98 ± 0.01
1.5	5	0.27 ± 0.01	0.22 ± 0.02	1.42 ± 0.02	0.96 ± 0.01
2.0	5	0.27 ± 0.02	0.22 ± 0.02	1.43 ± 0.02	0.83 ± 0.18
2.5	5	0.26 ± 0.01	0.22 ± 0.02	1.35 ± 0.02	0.83 ± 0.16

equivalency factors (TEF) of 0.1 and 0.01, respectively. The other compounds were not of significant importance due to their low TEFs (0.0001−0.0005). The values of TEQs for hot-smoked final products amounted to 0.22 ± 0.02 ng-TEQ/kg of wet weight (0.83 ± 0.16 ng-TEQ/kg of lipids) and 0.32 ± 0.02 ng-TEQ/kg of wet weight (1.32 ± 0.03 ng-TEQ/kg of lipids) for the cold-smoked ones.

Hot smoking also contributed to a drop of TEQ in the final product (mackerel slices) by 17.2%, whereas cold smoking produced an increase of TEQ by 31.7% in relation to initial raw material (**Figure 11**).

The assessment of consumer exposure risk through food is a weighty and difficult issue due to the fact that actual TEQ should also take into account other toxic compounds, such as polychlorinated dibenzo-*p*-dioxins (PCDDs), polychlorinated dibenzo-*p*-furans (PCDFs), and polychlorinated naphthalenes (PCNs). However, in the case of fish, polychlorinated biphenyls constitute >90% in total TEQ (*23*).

A common criterion used for the assessment of human exposure risk to residues of PCB compounds is the average daily intake of toxic substances per individual or per body weight (tolerable daily intake, TDI). On the basis of WHO's and FAO's settlements of July 2001 (*24*), TDI values for dioxins and dioxin-like compounds are 1−4 pg/day/kg of body weight. Taking into account the average annual consumption of fish (5.8 kg) in Poland in recent years (*25*) and TEQs determined for finished products after smoking for mackerel and herring, the average daily intake of toxic PCB congeners together with consumption of fish was counted. Assuming that cold-smoked mackerel with the highest average TEQ in finished product was mostly consumed, the average daily intake equaled 4.5 pg/day/person. In comparison with obligatory norms of the FAO and WHO for TDI being 60 pg/day/person, this value was considerably lower.

While evaluating the effect of smoking from the hygienic−sanitary point of view, one may judge that hot smoking is advisable for fish with high PCB content, as it reduces these compounds in the final products. This corresponds with the

earlier findings of Zabik et al. (*10*), who stated that from among thermal processing methods analyzed by them the highest drop of total PCB concentration (up to 39% in the final product) in the muscle tissue of lake trout occurred during hot smoking. Also, Salama et al. (*14*), while comparing several thermal processing methods, stated that hot smoking affected most effectively a decrease of total PCB content (65%) in the fillets of North Atlantic bluefish (*Pomatomus saltatrix*).

The reduction of PCB residues is still a current issue. Due to the high stabilities of these compounds, their long half-lives, and the possibility of their transport in the ecosystem via many routes, they find their way into food and thus to human organisms, who absorb them regularly, where they accumulate in tissues and organs. This is an unfavorable process from the point of view of human health. Therefore, use of all methods that may lower the amounts of absorbed PCBs and optimizing the selection of optimal methods for fish thermal processing connected with PCB reduction are still justified.

In conclusion, (1) hot smoking of mackerel slices contributed to lowering the content of analyzed non-*ortho* (PCB 77, PCB 126, PCB 169) and mono-*ortho* (PCB 114, PCB 156, PCB 157) congeners in the final products.

(2) During hot smoking, the largest losses in the contents of analyzed congeners in the wet muscle tissue of fish slices and in lipids were during the first hour of partial drying.

(3) Cold smoking of mackerel slices contributed to a small increase of the content of respective non-*ortho* and mono-*ortho* congeners in final products.

(4) The main factor determining the changes in the content of these compounds in the wet matter and when converted into lipids may have been their loss in codistillation with water vapor.

(5) In the final stages of hot smoking, a small increase was observed in the content of analyzed compounds due to the presence of PCBs in the smoke.

(6) Hot smoking of mackerel slices contributed to a drop of toxic dioxin equivalents (TEQ) in the final product by 17.9%, whereas it increased during cold smoking by 31.7% in relation to initial raw material.

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