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Effect of Hot Smoking on the Content of Selected Polychlorinated Biphenyl Congeners in Herring (*Clupea harengus*) Slices

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Herring (*Clupea harengus*) (as well as sprat and mackerel) is a fish species intensively harvested by the Polish fishing fleet. Its relatively low price and the habits of Polish consumers contribute to its high economic importance in Poland. Among 125.6 thousand tons of marine fish harvested in 2006, herring constituted 22.2 thousand tons (including 7.6 thousand tons harvested from the North Sea). Fish are usually subjected to various culinary treatments, which can influence the concentrations of contaminants in final products. Therefore, the present study aimed at determining the effect of three non-*ortho*-polychlorinated biphenyl (PCB) congeners (PCB 77, PCB 126, and PCB 169) and three mono-*ortho*-PCB congeners (PCB 114, PCB 156, and PCB 157) in the tissues of herring slices. Concentrations of dry matter and lipids in the final product were increased by 15.9 and 20.5%, respectively. Brining, which preceded the process of smoking, did not significantly influence concentrations of PCB congeners in herring slices. However, smoking resulted in significant ($p < 0.05$) changes in concentrations of three non-*ortho* PCBs. The biggest dynamics of losses in relation to smoking duration was observed for PCB 77 (30.2%). For PCB 126, the biggest losses occurred after 1 h of drying, followed by slight changes after 1.5 and 2 h of proper smoking and another increase of losses in the final product after 2.5 h. The duration of smoking did not significantly influence PCB concentrations in wet weigh, as their losses in lipids were much bigger. The observation is derived from strong negative correlations between concentrations of the congeners in lipids and lipid concentrations in herring slices during hot smoking (r ranging from –0.824 to –0.950). Although the lipid concentration in the smoked fish increased, the PCB content diminished. It shows that during drying of the fish slices, PCBs codistilled with water vapor, settling on the walls of the smoking chamber and smoking trolleys. During the proper smoking, the compounds released with the smoke back to the smoking chamber and settled on the surface of smoked fish together with the disperse phase of the smoke (aerosol). Hot smoking contributed to a reduction of toxic equivalents (TEQs) by 22.7% (converted into lipids 41.9%), and in the final product, it amounted to 0.0188 ± 0.0023 ng TEQ/kg of wet weight (0.0977 ± 0.0064 ng TEQ/kg of lipids). The reduction was significantly higher than resulting from hot smoking of mackerel slices, when TEQs were reduced by 17.9% wet weight (converted into lipids 31.7%).

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

INTRODUCTION

Persistent chlorinated compounds are some of the millions of chemicals present in the environment. The group contains polychlorinated biphenyls (PCBs), man-made chemicals, the production of which started at the beginning of the 20th century. PCBs are a mixture of congeners composed of two combined phenyl rings, with a varying number of chlorine atoms attached. They have low vapor pressure, but they can evaporate in codistillation with water vapor. Because of their good heat conductivity and dielectric properties, PCB mixtures have been used for a variety of industrial applications, mainly as dielectric fluids in electrotechnics, liquid heat exchangers, or lubricating and cutting oils.

Probably 2 million tons of PCBs have been manufactured globally. A side effect of the variety of their applications is that 1/3 of the total production has penetrated to the natural environment (*1*). Because PCBs occur in water and sediments of various water bodies, they are also detected in tissues of

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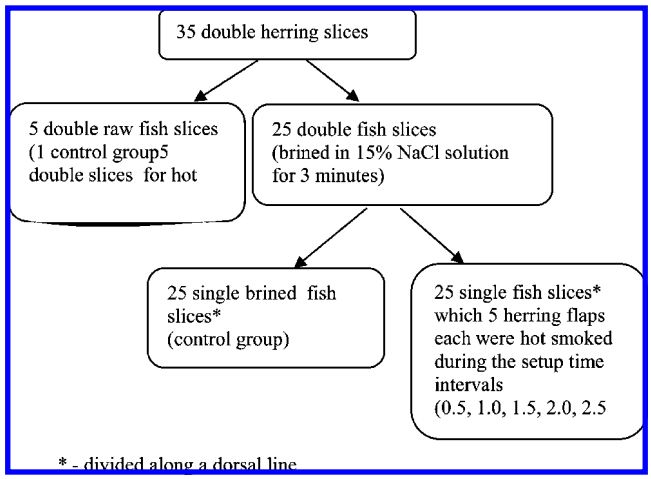

Figure 1. Scheme of the experiment.

aquatic animals, including fish, the fact being rather alarming for consumers.

Fish are usually consumed in a processed form, being previously subjected to a culinary treatment, which can influence the chemical composition of the final product. The problem has already been raised in other works (*2–5*). Most workers reported a loss of PCBs in examined products, resulting from a variety of heat treatment techniques. One of the techniques is smoking, widely used in Poland, especially for the processing of fish, cheeses, and cured meat. Herring (*Clupea harengus*) (as well as sprat and mackerel) is a fish species intensively harvested by the Polish fishing fleet. Its relatively low price and the habits of Polish consumers contribute to its high economic importance in Poland. Among 125.6 thousand tons of marine fish harvested in 2006, herring constituted 22.2 thousand tons, including 7.6 thousand tons harvested from the North Sea (*6, 7*).

The present study aimed at determining the effect of hot smoking on the content of toxic non-*ortho*- and mono-*ortho*-PCB congeners in herring slices. The study is a continuation and extension of our own studies on the effect of hot and cold smoking on PCBs in mackerel slices (*5*).

MATERIALS AND METHODS

Sampling. The material for analysis consisted of frozen double slices of herring (*C. harengus*) (according to the Polish Norm PN-A-86770). The research involved a raw material used at that time on the production line of a smoking plant. The fish were caught in the Norwegian Sea in September 2001. Smoking was carried out under industrial conditions in an "Atmos" type smoking chamber. The chamber was equipped with automatic temperature and humidity control and had a forced air circulation heating system. Salt (NaCl) was used as an auxiliary material. Smoke was produced from alder sawdust.

Prior to smoking, the herring slices were brined in 15% NaCl solution for 3 min. To determine changes during brining, five additional slices were split longitudinally into single slices, of which some were the control, and others were brined as a whole. After they were brined, batches of five double slices were sampled randomly and prepared for smoking. The double slices were cut into single slices, some of which were the control, prior to smoking, and others were hung on upper bars of smoking trolleys and were smoked for 0.5, 1.0, 1.5, 2.0, and 2.5 h (**Figure 1**).

Hot smoking was conducted analogically to the smoking of mackerel slices (*5*). It consisted of drying (1 h, 40 °C) and proper hot smoking, during which the smoke was supplied into the smoking chamber and the temperature was gradually raised to 80 °C.

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

Analytical Methods and Instrumentation. Analytical procedures and chromatographic analyses were conducted according to the methods described in ref *5*. Statistical testing included analysis of variance (Statistica 6.1 software package), calculation of correlation coefficients, and linear regression equations.

RESULTS AND DISCUSSION

Table 1 presents mean concentrations of examined compounds and standard deviations in raw herring slices, as well as in slices after brining and after subsequent stages of smoking. In the raw slices, the content of dry weight amounted to 33.45 ± 0.63%, and that of lipids amounted to 14.42 ± 0.21%. Hot smoking resulted in raising the dry weight content in the final product by 15.87% on average and the lipids by 20.54%.

The limit of quantification (LOQ) for the examined compounds was 0.02 ng kg^{-1} wet weight on the average, and it was the treble value of the LOD (limit of detection). The examinations were triplicated, and no significant differences ($p < 0.05$) were found between the findings. The recoveries of PCB congeners averaged as follows: PCB 77, 62.19 ± 4.27%; PCB 126, 71.08 ± 4.01%; PCB 169, 76.44 ± 1.89%; PCB 114, 76 ± 1.91%; PCB 156, 80 ± 2.17%; and PCB 157, 81.66 ± 2.64%. The obtained recovery of the pesticides surrogate spike mix ranged from 68 to 89%. Repeatability amounted to 1.79% on average and was determined by performing 10 quantitative determination of six congener standard solutions (Promochem GmbH, D 46485 Wesel) on concentration levels corresponding to the concentration in real samples.

Among all of the examined congeners, the greatest loss (up to 30.2% in dry matter of the final product) was observed for PCB 77, and the changes were statistically significant ($p < 0.05$) for all intervals (**Figure 2**).

For PCB 126, the highest significant decrease (33.3%) was observed during the proper hot smoking after 1.5 h, and a significantly lower decrease was observed after 2 (26.7%) and 2.5 h (24.3%) in the final product. When converted into concentration in the lipid fraction, its loss finally reached 41.9% (**Figure 2**).

PCB 169 also showed the highest losses during the proper hot smoking, followed by a slight increase. In the final product, it achieved a total decrease by 17.3% (30.2% in the lipid fraction). During the drying stage, concentrations of PCB 126 and PCB 169 in herring slices decreased, which resulted from the compounds' codistillation with water vapor. The fact is evidenced by simultaneous occurrence of their losses in both raw tissues and lipids. A slight increase of the congeners content during the following stage (proper smoking) was caused by their penetration into slices from the smoke.

The highest significant ($p < 0.05$) losses of PCB 114 were observed after 1 h of drying (27.9%), while hot smoking increased the concentration of the congener, so that the total decrease in the final product was only by 14.8% as compared to the initial value (**Figure 3**). Changes of the content of PCB 114 were not dependent on the duration of smoking process ($r_{w.w.} = -0.308$ and $r_{lip} = -0.662$). Statistically significant ($p < 0.05$) losses of PCB 156 and 157 were the biggest during drying, 26.4 and 12.5%, respectively, and in the final product, 21.6 and 18.3%, respectively.

The process of brining did not affect concentrations of examined congeners in herring slices. During the process of hot smoking, concentrations of the three non-*ortho*-PCB congeners changed significantly ($p < 0.05$), being correlated with the smoking duration, with changes of their concentration in the lipid fraction, and with changes of lipids in wet weight (**Figures 2** and **4**).

Table 1. Concentrations of Non-*ortho*- and Mono-*ortho*-PCB Congeners in Hot-Smoked Herring Slices

non-*ortho*-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/kg of wet weight)				
PCB 77	0.62 ± 0.06[a]	0.60 ± 0.06	0.54 ± 0.05	0.51 ± 0.01	0.42 ± 0.02	0.45 ± 0.06	0.44 ± 0.03
PCB 126	0.18 ± 0.03	0.17 ± 0.09	0.16 ± 0.06	0.14 ± 0.02	0.12 ± 0.04	0.14 ± 0.01	0.14 ± 0.02
PCB 169	0.21 ± 0.05	0.19 ± 0.03	0.16 ± 0.01	0.12 ± 0.02	0.13 ± 0.03	0.15 ± 0.03	0.15 ± 0.01
			content (ng/kg of lipids)				
PCB 77	4.33 ± 0.17	4.25 ± 0.19	3.55 ± 0.12	2.81 ± 0.11	2.36 ± 0.11	2.47 ± 0.11	2.44 ± 0.11
PCB 126	1.25 ± 0.29	1.13 ± 0.17	1.05 ± 0.18	0.86 ± 0.03	0.67 ± 0.05	0.70 ± 0.09	0.73 ± 0.05
PCB 169	1.46 ± 0.22	1.35 ± 0.14	1.05 ± 0.17	0.69 ± 0.09	0.73 ± 0.08	0.82 ± 0.04	0.83 ± 0.08

mono-*ortho*-congeners	before brining	after brining (3 min)	smoking duration (h) 0.5	1	1.5	2	2.5 (final product)
			content (ng/kg of wet weight)				
PCB 114	0.80 ± 0.04	0.77 ± 0.03	0.66 ± 0.05	0.57 ± 0.08	0.61 ± 0.04	0.66 ± 0.08	0.69 ± 0.01
PCB 156	5.98 ± 0.25	5.77 ± 0.31	4.27 ± 0.22	4.11 ± 0.15	4.35 ± 0.17	4.63 ± 0.16	4.77 ± 0.23
PCB 157	1.31 ± 0.21	1.26 ± 0.13	1.12 ± 0.15	0.98 ± 0.09	1.05 ± 0.09	1.04 ± 0.19	1.12 ± 0.21
			content (ng/kg of lipids)				
PCB 114	5.55 ± 0.09	5.45 ± 0.19	4.34 ± 0.08	3.29 ± 0.29	3.42 ± 0.23	3.62 ± 0.23	3.83 ± 0.29
PCB 156	41.47 ± 1.01	40.86 ± 1.99	28.09 ± 0.94	23.69 ± 0.42	24.43 ± 0.20	25.38 ± 0.96	26.47 ± 0.61
PCB 157	9.08 ± 0.38	8.92 ± 0.34	7.37 ± 0.17	5.07 ± 0.16	5.89 ± 0.18	5.70 ± 0.28	6.20 ± 0.37

[a] The average content of a PCB congener ± standard deviation.

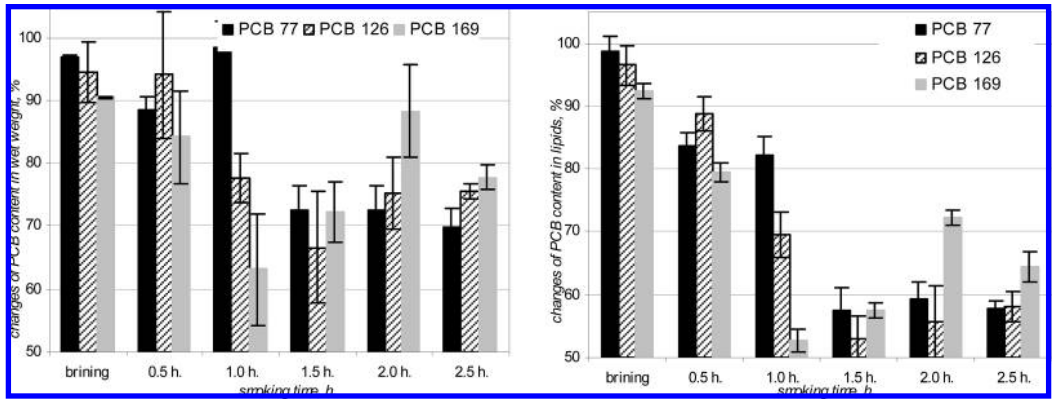

Figure 2. Percentage changes in the content of non--*ortho*--PCB congeners in herring slices during hot smoking.

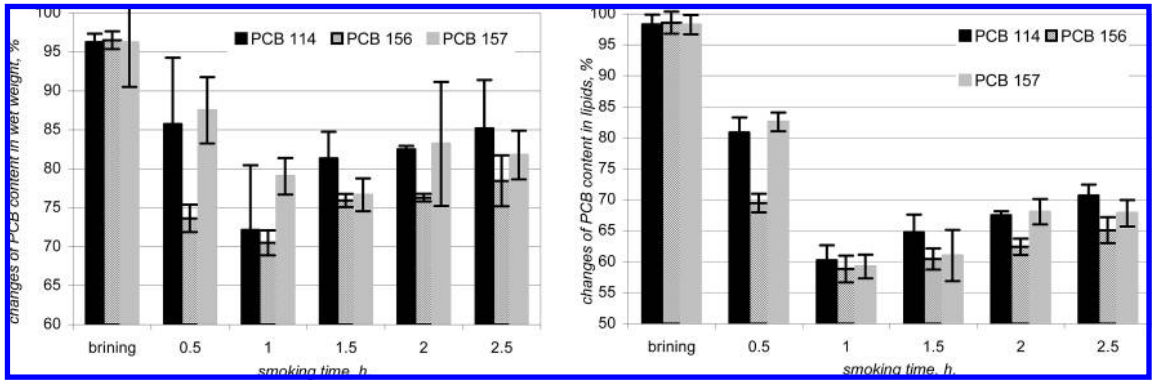

Figure 3. Percentage changes in the content of mono-*ortho*-PCB congeners in herring slices during hot smoking.

During hot smoking of herring slices, similarly as in the case of mackerel slices (*5*), PCB 77 was the congener that showed the biggest dynamics of losses in wet weight and in the lipid fraction, the losses being dependent on the smoking duration. Its concentrations in fish slices constantly decreased during the whole smoking cycle. As the congener was not detected in the alder sawdust and the smoke (*5*), it did not penetrate into the herring slices from the smoke, as was the case in the other examined congeners. PCB 77 (3,3′,4,4′-tetrachloroPCB) has only four chlorine atoms in a molecule and is characterized by a higher vapor pressure. Therefore, it easily volatilized in codistillation with water vapor (*8*), and the temperature of the heat treatment influenced its volatilization rate (*9*). Moreover, as reported in refs *10–12*, PCBs are quite stable thermally and do not get degraded at temperatures below 200 °C. For these reasons, their losses during technological and culinary treatments depend mainly on the temperature applied, on the duration of the treatment, and on changes in lipid concentration (*9*).

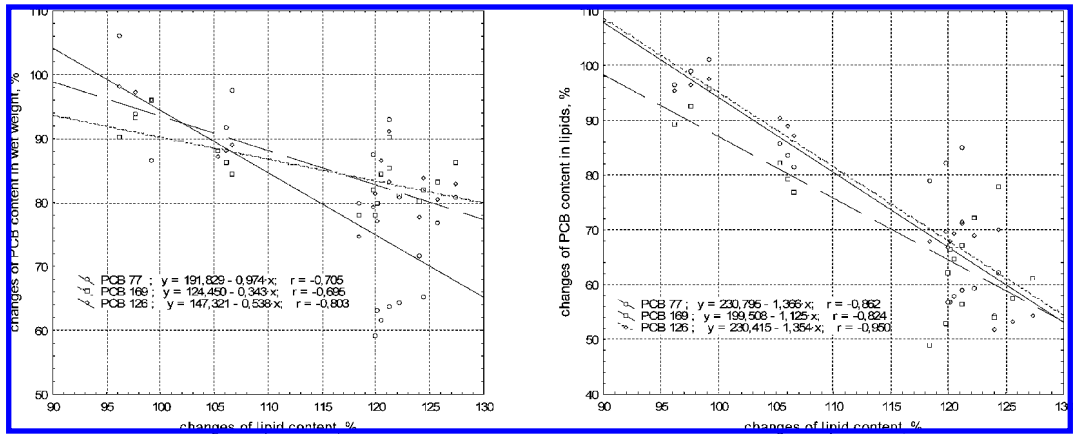

Figure 4. Correlations between percentage changes of non-*ortho*-PCB congeners and lipids in hot-smoked herring slices.

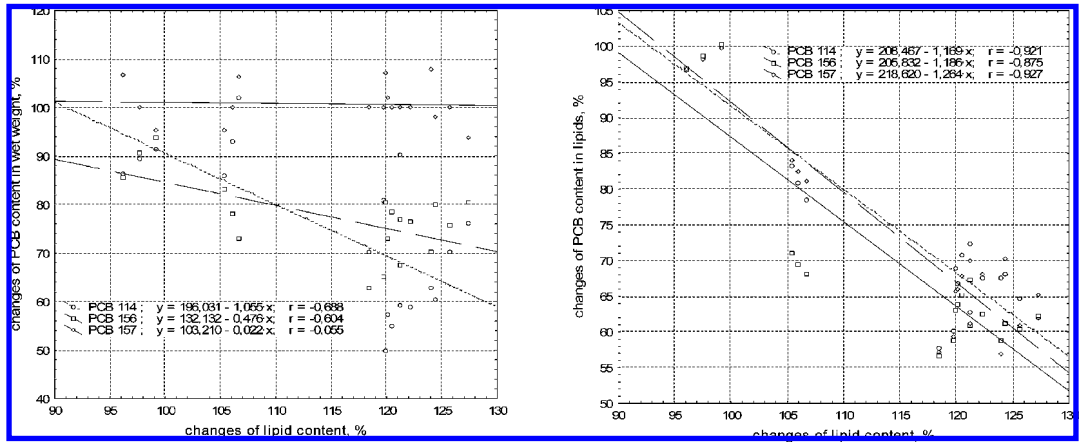

Figure 5. Correlations between percentage changes of mono-*ortho*-PCB congeners and lipids in hot-smoked herring slices.

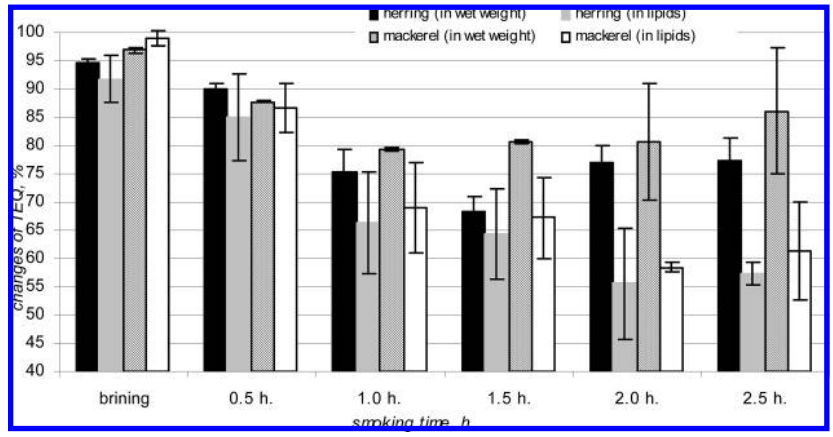

Figure 6. Changes of TEQs relative to the duration of smoking: hot-smoked mackerel and herring.

In the experiment, the biggest losses of PCB 126 occurred after 1 h of drying. During the first 2 h of the proper smoking, some smaller losses were also observed, but after 2.5 h of hot smoking, the PCB 126 content in the final product was slightly raised. Therefore, the duration of hot smoking was weakly correlated with losses in wet weight ($r = -0.40$); however, they were significantly correlated with losses in the lipid fraction ($r = -0.72$).

The main factor that determined changes in the concentrations of the examined PCB congeners in the wet matter and in the lipid fraction was their codistillation with water vapor. During drying, the compounds settled on smoking trolleys and on the walls of the smoking chamber. During the proper hot smoking, they were released with the smoke back to the smoking chamber and settled on the surface of the smoked fish slices together with the disperse phase (aerosol) of the smoke.

A review of works on the influence of fish processing on PCB content shows that processes of coking, roasting, grilling, and smoking significantly reduce the total contents of PCBs or contents of indicator PCBs in the product processed. The changes depend mainly on the lipid content, the kind of process applied, temperature, duration of the process, and the method of sample preparation (e.g., fillets with skin or without skin) (*2–5, 13*). The losses observed ranged from several to several dozen percent.

The duration of smoking did not significantly influence PCB concentrations in wet weight, as their losses in lipids were much bigger. The observation is derived from strong negative correlations

between concentrations of the congeners in lipids and lipid concentrations in herring slices during hot smoking (r ranging from –0.824 to –0.950) (**Figures 4** and **5**). Although the lipid concentration in the smoked fish increased, the PCB content diminished. It shows that during drying of the fish slices, PCBs codistilled with water vapor and settled on the walls of smoking chamber and smoking trolleys. During the proper smoking, the compounds released with the smoke back to the smoking chamber and settled on the surface of smoked fish together with the disperse phase of the smoke (aerosol). The thesis was confirmed by the analysis of saw dust used for smoking and by the experiment with absorbent paper strips soaked in soybean oil and placed in the smoking chamber among the fish slices (*5*).

To determine the health risk connected with the consumption of hot-smoked herring slices, after each stage of smoking, toxic equivalents (TEQs) were calculated as a sum of products of concentrations of individual congeners and their toxic equivalency factors (TEFs) (*14*). In raw brined herring slices, mean TEQ values amounted to 0.0239 ± 0.0033 ng TEQ/kg of wet weight, and converted into lipids, they amounted to 0.1735 ± 0.0214 ng TEQ/kg (**Figure 6**). The values of TEQs for hot-smoked final products amounted to 0.0188 ± 0.0023 ng TEQ/kg of wet weight (0.0977 ± 0.0064 ng TEQ/kg of lipids). The comparison leads to the conclusion that hot smoking contributed to a reduction of TEQ in the final product by 22.7% (41.9% in lipids) in relation to the initial raw material.

TEQ losses during hot smoking of herring slices were significantly higher than during hot smoking of mackerel slices (*5*), especially in the last stage of smoking. This probably resulted from the texture and size of the smoked slices. Herring slices were smaller and nearly twice as thin as the mackerel fillets and had a looser texture. Therefore, the ratio of their surface area to their mass or volume was bigger. During thermal processing, this could contribute to easier penetration of chemicals from the smoke into the tissue but also to easier escape of chemical compounds from the tissue.

In both mackerel (*5*) and herring hot-smoked slices, weak negative correlations were found between the changes of TEQs and the duration of smoking. The TEQ values in the final products reflected mainly changes in concentrations of two congeners: PCB 126 and PCB 169 (TEF values, 0.1 and 0.01, respectively).

Taking into account the average annual consumption of fish (5.8 kg) in Poland in recent years (*15*) and TEQs determined for the hot-smoked herring slices (0.0188 ± 0.0023 ng TEQ/kg of wet weight), the average daily intake of PCBs was calculated and amounted to 0.005 pg TEQ/kg of body weight/day. An assumption was made that only the analyzed hot-smoked herring slices were consumed. The obtained value was low, as compared with the value of tolerable daily intake settled on by the WHO and FAO: 1–4 pg/day/kg of body weight.

The following conclusions have been made:

1. Hot smoking of herring slices reduced the content of analyzed non-*ortho*- (PCB 77, PCB 126, and PCB 169) and mono-*ortho*- (PCB 114, PCB 156, and PCB 157) congeners in the final products.
2. The main factor determining the changes of these compounds in the wet matter and in the lipid fraction was their codistillation with water vapor. During drying, the compounds settled on the smoking trolleys and on the walls of the smoking chamber. During the proper hot smoking, they were released with the smoke back to the smoking chamber and settled on the surface of the smoked fish together with the disperse phase (aerosol) of the smoke (increase of the concentrations of the analyzed PCB compounds resulting from their presence in the smoke).
3. Changes in the TEQs for the hot-smoked herring slices (in relation to dioxin 2,3,7,8-TCDD) were derived mainly from the changes of concentrations of PCB 126 and PCB 169. In the final product of smoking, TEQ amounted to 0.0188 ± 0.0023 ng TEQ/kg of wet weight (0.0977 ± 0.0064 ng TEQ/kg of lipids).
4. Hot smoking of herring slices contributed to a reduction of TEQ in the final product by 22.7% (converted into lipids 41.9%). The reduction was significantly higher than resulting from hot smoking of mackerel slices, when TEQs were reduced by 17.9% wet weight (converted into lipids 31.7%).

LITERATURE CITED

(1) Hansen, L. G. Environmental toxicology of polychlorinated biphenyls. In *Environmental Toxin Series 1. Polychlorinated Biphenyls (PCBs): Mammalian and Environmental Toxicology*; Safe, S., Ed.; Springer-Verlag: Berlin, Heidelberg, 1987; Vol. 1, pp 5–48.

(2) Zabik, M. E.; Booren, A.; Zabik, M. J.; Welch, R.; Humphrey, H. Pesticide residues, PCBs and PAHs in baked, charbroiled, salt boiled and smoked Great Lakes lake trout. *Food Chem.* **1996**, *55* (3), 231–239.

(3) Salama, A. A.; Mohamed, M. A. M.; Duval, B.; Potter, T. L.; Levin, R. E. Polychlorinated biphenyls concentration in raw and cooked North Atlantic Bluefish (*Pomatomus saltatrix*) fillets. *J. Agric. Food Chem.* **1998**, *46*, 1359–1362.

(4) Ciereszko, W.; Witczak, A. Changes of the content of selected PCB congeners in carp meat as a result of cooking. *Acta Sci. Pol. Technol. Aliment.* **2003**, *2* (1), 155–164.

(5) Witczak, A.; Ciereszko, A. The effect of smoking process on changes in the content of selected non-*ortho* and mono -ortho PCB congeners in mackerel slices. *J. Agric. Food Chem.* **2006**, *54* (15), 5664–567.

(6) *Concise Statistical Yearbook of Poland*; Editorial Board of Central Statistical Office: Warsaw, 2007.

(7) *Statistical Yearbook of Maritime Economy*; Central Statistical Office, Statistical Office in Szczecin: Warszawa-Szczecin, 2007.

(8) Wania, F.; Mackay, D. Tracking the distribution of persistent organic pollutants. *Environ. Sci. Technol.* **1996**, *30*, 390A–396A.

(9) Sherer, R. A.; Price, P. S. The effect of cooking processes on PCB levels in edible fish tissue. *Qual. Assur., San Diego* **1993**, *2*, 396–407.

(10) Morita, M.; Nakagawa, J.; Rappe, C. Polychlorinated dibenzofuran (PCDF) formation from PCB mixture by heat and oxygen. *Bull. Environ. Contam. Toxicol.* **1978**, *18*, 67–78.

(11) Gidlund, M. Photochemical and thermal stability of polychlorinated biphenyls (PCBs). M.Sc. Thesis, Umea University, MKD, 1995; Vol. 95, p 5.

(12) Hansen, L. G. *The Ortho-Side of PCBs: Occurrence and Disposition*; Kluwer Academic: Norwell, MA, 1999.

(13) Witczak, A.; Ciereszko, A. Changes in total PCB content in selected fish products during hot- and cold smoking. *Acta Ichthyol. Piscatoria* **2006**, *36* (1), 11–16.

(14) Van den Berg, M.; Birnbaum, L.; Bosveld, A. T. C.; Brunström, B.; Cook, P.; Feeley, M.; Giesy, J. P.; Hanberg, A.; Hasegawa, R.; Kennedy, S. W.; Kubiak, T.; Larsen, J. C.; van Leeuwen, F. X. R.; Liem, A. K. D.; Nolt, C.; Peterson, R. E.; Poellinger, L.; Safe, S.; Schrenk, D.; Tillitt, D.; Tysklind, M.; Younes, M.; Waern, F.; Zacharewski, T. Toxic Equivalency Factors (TEFs) for PCBs, PCDDs, PCDFs for humans and wildlife. *Environ. Health Perspect.* **1998**, *106* (12), 775–792.

(15) *Statistical Yearbook of Maritime Economy*; Central Statistical Office: Warsaw, Poland, 2004.

(16) Kurko, W. I. *Chemical and Physicochemical Basis of Smoking Process*; Publishing Company of Light Industry and Food Processing Industry: Warszawa, 1963.

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