Fish products available in Polish market – Assessment of the nutritive value and human exposure to dioxins and other contaminants

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Abstract

Chemical analyses were performed on one hundred and twenty of the most popular varieties of fish products (smoked fish, salted fish, and marinated fish) of the fish market in Poland. The contents of the nutritive substances of fish products (protein, micro- and macronutrients, vitamins A, D, E, and fatty acids) and the chosen contaminant (toxic metals – mercury, cadmium, lead, arsenic; dioxin/furans – PCDDFs; dioxin-like PCB – dl-PCBs; seven congeners of polybrominated diphenyl ethers – PBDEs; organochlorine pesticides – ΣDDT, HCB, ΣCHC and marker polychlorinated biphenyls – PCB28) levels were determined.

It was confirmed that fish products are a good source of digestible proteins, iodine, selenium, and vitamin D3. The fundamental nutritive benefit of processed fish lies in its highly beneficial fatty acid composition, which is what imparts them healthy nutritive qualities. The high content of long-chain polyunsaturated fatty acids (LC-PUFAs), which is not noted in other food products, is particularly important.

The majority of contaminants studied were present in low levels. The possible threats, particularly in the case of pregnant/nursing women and young children, can pose the levels of dioxin/furans (PCDD/Fs) and dioxin-like (dl-PCBs) in smoked Baltic salmon and smoked sprat, elevated in a relation to particular requirements concerning the content of sum of PCDD/Fs and dl-PCBs in fish (8 pg WHO-TEQ g⁻¹). The health benefits and risks stemming from consumption of fish products were determined according to the Provisional Tolerable Weekly Intake (PTWI) for chosen contaminants (Cd, Hg, As, PCDD/Fs + dl-PCBs) and the quantity of ingredients that render a fish diet healthy based on data from the EFSA Journal [EFSA (European Food Safety Authority), 2005. Opinion of the scientific panel on contaminants in the food chain on a request from the European Parliament related to the safety assessment of wild and farmed fish. EFSA J. 236, 1–118]. In regard of high content of LC-PUFAs and other nutritive ingredients, fish products available in Polish market may be considered as healthy food.

However, many authors point at contaminants (methylmercury, PCDD/Fs) occurring in fish and fish products as on potential health problem, and emphasize that the amount of that hazardous substances should be limited in human diet.

1. Introduction

The consumption of fish and fish products is recommended as a means of preventing cardiovascular and other diseases and has greatly increased over recent decades in many European countries (Cahu et al., 2004). Compared with other European countries, the consumption of fish and fish products in Poland is very low (e.g. 9-fold lower than in Portugal).

The proper human diet should satisfy the requirements for energy and nutritive components including: essential polyunsaturated fatty acids, exogenous amino acids being the component of standard proteins, mineral components, fat, and water-soluble vitamins. Fish and fish products are characterized by the significant content of the above-mentioned components. However, the most important feature of this food is an advantageous fatty acid profile, resulting from the high content of essential polyunsaturated fatty acids such as eicosapentaenoic (C20:5 n-3) and docosahexaenoic (C22:6 n-3) (Kris-Etherton et al., 2002).

In recent years, investigations aimed at identifying the benefits of fish consumption have also indicated that there are risks connected with toxic contaminants such as methylmercury and persistent organic pollutants (first of all dioxin-like dl-PCBs and PCDD/Fs) (Mahaffey, 2004; Domingo et al., 2007a,b; Stern, 2007; Wu et al., 2008; Szlinder-Richert et al., 2008a,b,c).
In a recent investigation concerning canned fish and other fish products, we showed that these products are characterized by high nutritional quality and that considering the present scenario of the fish consumption in Poland, they do not pose a threat for Polish consumers due to the contaminant levels (Usydus et al., 2008, 2009).

The aim of the current study was to conduct tests to determine the quantity of the healthy components and toxic substances in smoked, salted, and marinated fish products. That products together with canned fish account for as much as 60% of the fish consumed in Poland (on average approximately 3.8 kg per capita annually). Through this study, the authors would like to join in the general discussion of the risks and benefits of consuming fish and fish products.

2. Materials and methods

2.1. Sampling for testing

Samples were taken during the period: January–November of 2006. These were the most popular of the fish products in the Polish market. The samples were purchased from large supermarkets, grocery stores, or directly from the manufacturers and originated from the biggest manufacturers of fish products in Poland, whose plants are situated in the following provinces: Pomorskie, Zachodnio-Pomorskie, Śląskie, Wielkopolskie. These products are distributed in whole Poland. As much as 1200 individual samples were taken and 120 composite samples were prepared and analyzed. Each composite sample consisted of ten individual samples. Each assortment was represented by ten composite samples, and sampling was carried out in such way that each composite sample was characterized by different date of production. The following assortments of fish products were chosen for testing:

<table>
<thead>
<tr>
<th>Smoked fish</th>
<th>Salted fish</th>
<th>Marinated fish</th>
</tr>
</thead>
<tbody>
<tr>
<td>2. Smoked sprat</td>
<td></td>
<td>9. Fried Mackerel in vinegar</td>
</tr>
<tr>
<td>3. Smoked herring</td>
<td></td>
<td></td>
</tr>
<tr>
<td>4. Smoked Baltic salmon</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5. Smoked Norwegian salmon /farmed/</td>
<td></td>
<td></td>
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<tr>
<td>6. Smoked trout</td>
<td></td>
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</tr>
</tbody>
</table>

Mackerel, sprat, herring, and trout were hot-smoked and salmon was cold-smoked.

The health benefits and risks stemming from consumption of fish products were determined according to the Provisional Tolerable Weekly Intake (PTWI) for contaminants and according to the quantity of ingredients that render a fish diet healthy based on data from the EFSA Journal (2005).

2.2. Study methods

The majority of the chemical testing was performed at the Accredited Testing Laboratory of the Sea Fisheries Institute in Gdynia. The analyses were conducted using validated methods according to the testing procedures that are binding on the laboratory (Accreditation Certificate No. AB 017 awarded by the Polish Center of Accreditation in accordance with PN-EN ISO/IEC 17025:2001 standard based on PN-EN ISO 8294 and PN-EN ISO 12193 standards).

The tests were performed as described below:

**Mineral components** – were determined with atomic absorption spectrometry. The following micro and macronutrients (calcium – Ca, phosphorous – P, selenium – Se, fluoride – F, iodine – I), and toxic metals (mercury – Hg, cadmium – Cd, lead – Pb, and arsenic – As) were determined. Samples for testing the contents of most of the elements were wet mineralized with concentrated nitric acid in MD-2100 microwave ovens (CEM Corporation) and the final determinations were performed with the atomic absorption method in a graphite furnace with a Perkin Elmer 4100 atomic absorption spectrometer with plasma excitation using a VISTA-MPX emission spectrometer. Mercury analysis was performed with flameless atomic absorption spectrometry using an Altec AMA-254 spectrophotometer. Iodine and fluoride contents were assayed at the Accredited Chemical Laboratory of Multielemental Analyses at the Wrocław University of Technology. Iodine was determined by spectrometric method using the ICP-OES technique, and fluoride was measured by means of ion-selective electrode.

**Quality control/assurance.** Certified reference material MR-422 (cod muscle) containing Pb at concentration of 0.085 mg kg⁻¹ ± 0.016 and Cd at concentration of 0.017 mg kg⁻¹ ± 0.002 was used for quality assurance in determination of Pb and Cd. In determination of As and Hg certified reference materials (Lobster Hepatopancreas) LUTUS 1 and TORT 2 containing As at concentration of 2.83 mg kg⁻¹ ± 0.13 and Hg at concentration of 0.27 mg kg⁻¹ ± 0.06 were used. The laboratory has participated in international intercalibration trials organized by: International Atomic Energy Agency – Marine Environment Laboratories (IEAE-MEL) in Monaco, European Commission Joint Research Centre in Belgium and Państwowy Zakład Higieny in Warsaw, and has achieved positive results (e.g. z-score for Cd, Pb, As and Hg – 0.61, –0.61, 0.59 and –0.51, respectively).

**Fat-soluble vitamins** (A₁ – all-trans-retinol, D₃ – cholecalciferol, E – α-tocopherol). Freeze-dried samples were saponificated and vitamins were extracted with hexane. Extracts were evaporated and the residue was dissolved in methanol. Final determination was performed using HPLC technique. Vitamins A and E were determined with using fluorescence and vitamin D₃ with using UV detector. Quantification of vitamin A and E was performed on the basis of area of standard peaks, while vitamin D₃ was determined with using of vitamin D₂ as internal standard; internal standard was added to samples prior to saponification.

**Quality control/assurance.** Certified reference materials: Baby Food Composite 2383 and Margarine CRM 122 were used for method validation and quality control. Recoveries of vitamins from that materials were: vit A: 105% (Baby Food Composite 2383) and 85% (Margarine CRM 122); vit E: 70.5% (Baby Food Composite 2383) and 81% (Margarine CRM 122); vit D₃: 110% (Margarine CRM 122). One of each twenty samples was analyzed in two parallel determinations. Certified reference material is analyzed at least four time a year. The SFI’s laboratory participated with the satisfying results in the intercalibration trials organized by FAPAS.

**Organochlorine pesticides** (hexachlorocyclohexane isomers – α-, β-, γ-HCH; hexachlorobenzene – HCB; 1,1,1-trichloro-2,2-bis(4-chlorophenyl)ethane – pp'-DDT and DDT metabolites, 1,1,2-trichloro-2,2-bis(4-chlorophenyl)ethane – pp'-DDD; 1,1-dichloro-2,2-bis(4-chlorophenyl)ethylene – pp'-DDE) and seven marker polychlorinated biphenyls – PCB₇ (IUPAC nos. 28, 52, 101, 118, 138, 153 and 180). Freeze-dried samples were extracted with n-hexane in the Soxtec Avanti apparatus (FOSS), during 4 h. The solvent was carefully evaporated and the fat content was determined gravimetrically. An aliquot of lipids (0.5 g of oil) was dissolved in n-hexane in stopped glass tubes and treated with a mixture of concentrated sulphuric acid and 30% fuming sulphuric acid at a ratio 1:1 v/v and periodically shaken.
during 3 h. After centrifugation samples were frozen and an upper solvent phase was collected. A sulphuric acid phase was defrosted, and reextracted with hexane. Combined extracts were adjusted to volume of 1 ml and analyzed using FISONS 8000 series gas chromatograph (GC) equipped with AS 800 autosampler and an electron capture detector (ECD) and Rtx-5 column 60 m in length was used.

Quantification was carried out on the basis of area of standard peaks. Measurements were carried out within the linear range of the detector.

Quality control/assurance. The SFI’s laboratory annually participates with the satisfying results in the intercalibration trials organized by: QUASIMEME, IAEA, FAPAS and Państwowy Zakład Higieny (PZH) in Warsaw.

Quality assurance of each series of analysis (10 samples) was secured through parallel analysis of standard solutions, a home-made material (freeze-dried herring tissue) and blank samples. Blanks did not contain traces of analytes or their levels were so low in comparison with levels in analyzed extracts that amounts from blanks were not subtracted from samples. A one sample of each series was analyzed in three replicates.

Recoveries of organochlorine pesticides from certified reference material CRM 1588a (cod liver oil) were: α-HCH 62%; γ-HCH 72%; HCB 75%; DDE 76%; DDD 80%; DDT 108%.


For results below the LOQ, a value equal to half of the limit was assigned.

Fatty acids – freeze-dried samples were extracted with mixture of (4:1) hexane:acetone in the Soxtec Avanti apparatus, during 4 h. The chromatographic analysis of the fatty acids was performed after they had been passed through the appropriate methyl ester. Following esterification, fatty acids were extracted with isooctane; extracts were diluted with methanol and analyzed with the GC/FID technique with the help of a Supelco SP 2560 column of a length of 100 m. Identification and quantification were performed on the basis of retention times and are of peaks in standard mixture (39 compounds). The SFI’s laboratory participated with the satisfying results in the intercalibration trials organized by: FAPAS.

Basic nutritional components – (dry weight, overall protein, fat, chlorides, ash, digestible protein) – were determined at the SFI Accredited Laboratory based on Polish standards and the methodology outlined in AOAC [1990].

PCDD/Fs, dl-PCBs, and PBDEs – polychlorinated dibenzo-paratrichlorins (PCDDs - the sum of seven most toxic congeners), polychlorinated dibenzofurans (PCDFs – the sum of ten most toxic congeners), dioxin-like PCBs (dl-PCBs - the sum of four non-ortho PCB nos. 77, 81, 126, 169 and the sum of eight mono-ortho PCB nos. 105, 114, 118, 123, 156, 157, 167, 189), which were designated in 1998 by the WHO as a group of PCBs that should be analyzed together with PCDD/F and polylabeled diphenyl ether (PBDEs– the sum of seven congeners–BDE-28, BDE-47, BDE-100, BDE-99, BDE-154, BDE-153, and BDE-183, which are usually found in fish (de Wit, 2002; Parmanne et al., 2006). The tests were conducted at the Accredited Laboratory of the Institute of Public Health in Ostrava, Czech Republic. Samples were homogenized, freeze-dried, fine-ground and extracted with n-hexane in the Soxtec Avanti apparatus (FOSS). The solvent was carefully evaporated and the lipid content was determined gravimetrically. Fat was removed by dialyzation on SPM, and clean up was performed using adsorption chromatography with the following sequence of adsorbents: I – acid and basic silica gel; II – acid and basic alumina; III – activated carbon. The analyses were performed on Finningan MAT 95X high resolution mass spectrometer (operating at resolution 10000 or higher), which was connected with gas chromatograph Agilent 6890 (Agilent Technologies, USA); DB5ms (30 m × 0.25 mm × 0.25 μm) column was used. Calibration and verification standard mixtures EN 1948 CS1-CS6 (Wellington Laboratories, Canada), and reference material WMF-01 (freeze-dried fish tissue) were used for validation. Samples were spiked with the mixtures of the isotope labeled standards.

Quantification limits varied depending on congener and sample size. The concentrations below the limits of quantification (LOQs) were equated to half of the LOQ, PCDD/Fs and dl-PCBs content is expressed as TEQ values, which were calculated for each sample by multiplying the individual congener levels measured in each sample with the appropriate Toxic Equivalency Factor (TEF). The TEF used were established by the World Health Organization (WHO) for humans and are calculated relative to 2,3,7,8-TCDD (van den Berg et al., 1998).

3. Results and discussion

3.1. Basic nutritional ingredients

The fish products tested are a good source of highly digestible protein. The highest average protein content (Table 1) was measured in smoked trout (23.34%) and the lowest in marinated herring fillets (12.81%). The protein in the fish products tested was of a high quality as over 96% of it was digestible. An average fat content in fish products tested ranged between 6.06% (smoked trout) and 20.76% (smoked mackerel). Fats are the most concentrated source of energy, and in addition, fish fat is a very good source of essential unsaturated fatty acids (EUFAs).

3.2. Composition of fatty acids

Table 2 shows the percentage composition of fatty acids in lipids extracted from fish products. The amounts of 32 fatty acids were determined. Unidentified fatty acids accounted for 8.5% (salted herring fillets) to 14.2% (smoked trout). The assessed EPA + DHA content expressed in mg 100 g−1 of product for particular group of products are shown in Table 1, and Table 3 shows the amounts of particular products, which cover the daily amounts of these acids recommended for the prevention of heart diseases.

The composition of fatty acids of fish products were found to be 19.4–29.3% saturated (SFAs), 30.9–54.4% monounsaturated (MUFA), and 14.2–34.0% polyunsaturated (PUFAs). The highest share of PUFAs and acids from the n-3 family was noted in lipids extracted from smoked Baltic salmon (34.0% and 24.1%, respectively) and the lowest in lipids extracted from smoked herring (14.2% and 10.6%, respectively). The ratio of acids from n-6 and n-3 family: n-6/n-3 was lower than 1 (ranging from 0.32 in smoked sprat to 0.74 in smoked trout) in all the fish products tested.

The ratio of n-6/n-3 in human diet is an important factor. The justification for applying that factor as a predictor for coronary artery events, results from the fact that the ratio of these fatty acids in the human diet is estimated to have increased over the millennia from approximately 1:1 to 20–25:1 and the fact that these two classes of fatty acids compete for the same metabolic pathways (Block and Pearson, 2006). This dramatic dietary shift is thought to be related to reduction in fish consumption of domestically raised fish (DeFillippies and Sperling, 2006). The recent investigation did not lead to the determination of the n-6/n-3 ratio as being appropriate for the lowering of the risk of coronary heart disease (CHD). However, current evidence supports two strategies for lowering CHD risk: replacement of saturated and trans fatty acids with cis-, poly-, or monounsaturated fatty acids, and increasing absolute intake of n-3 fatty acids from plant sources and fish. These two strategies can be complementary and will have the potential to
maximize the cardio-protective benefits of dietary fatty acids (Hu, 2001; Harris et al., 2006). It means that the low ratio of n-6/n-3 acids (below 1) in the fish products in Polish market is beneficial because it helps to enrich the diet of an average Pole with acids from n-3 family.

A minimum value of PUFA/SFA ratio recommended by UK Department of Health is 0.45 (HMCO, 1994), which was lower than those obtained for all the fish products studied. PUFA/SFA ratio of the studied fish products ranged from 0.67 for smoked herring to 1.44 for smoked Baltic salmon.

The most significant benefits resulting from consumption of fish and fish products is attributed to the high content of polysaturated fatty acids, particularly EPA and DHA (which is not found in other food products), which have protective effects in the prevention of cardiovascular disease – CVD (Kris-Etherton et al., 2002). Among the samples studied, the highest contents of these acids were found in: smoked mackerel (2926 mg 100 g⁻¹ of product), smoked sprat (2422 mg 100 g⁻¹), and fried mackerel in vinegar (2026 mg 100 g⁻¹). The lowest amounts of these acids were found in smoked herring (708 mg 100 g⁻¹) and in smoked trout (860 mg 100 g⁻¹).

The American Heart Association (AHA), in its 2003 recommendations, suggests that people with known coronary heart disease (CHD) should consume approximately 1 g of EPA and DHA each day (AHANC, 2006). People without any symptoms of CVD should consume approximately 500 mg of these acids daily for prophylactic purposes. The higher doses of these acids lower the very high triglycerides levels found in blood (AHANC, 2006). AHA recommendations report that intake of approximately 2–4 g of EPA + DHA each day may lower triglycerides by 20–40% (Kris-Etherton et al., 2003). However, due to the risk of bleeding resulting from the intake of n-3 fatty acids (particularly at doses greater than 3 g d⁻¹), a physician should be consulted before starting treatment with this dose (Kris-Etherton et al., 2002).

On the basis of the study conducted, we can conclude that the fish products in Polish market are a good source of beneficial fatty acids. As little as 34 g of smoked mackerel meets the daily allowance of EPA and DHA recommended for person with symptoms of CVD. Half of these amount will supply the recommended daily allowance of EPA and DHA in case of persons without symptoms of CVD. The evidence across the different studies of Mozaffarian and Rimm (2006) showed that fish consumption lowers the risk of death from heart disease by 36%. The benefit was related to the level of intake of omega-3 fatty acids, and thus benefits are greater for oily fish, which are higher in beneficial omega-3 fatty acids, than lean fish. They also found that fish or fish oil intake reduces total mortality by 17%, a remarkable reduction considering that this is the benefit for deaths from all causes.

3.3. Fat-soluble vitamins

The average contents of vitamins A₁, D₃, and E are shown in Table 1. The highest levels of these vitamins (A₁, D₃, and E) were found in smoked sprat (432 µg 100 g⁻¹), smoked herring (15.8 µg 100 g⁻¹), and Norwegian smoked salmon (2095 µg 100 g⁻¹). In the remaining products, the concentrations of vitamin A₁ was more than 10-fold lower. The lowest amounts of vitamin E were measured in products made from mackerel (smoked mackerel – 164 µg 100 g⁻¹, fried mackerel in vinegar – 235 µg 100 g⁻¹). The products examined contained significant levels of vitamin D₃ in comparison with the recommended daily allowance for adults (Ladipo, 1998; Zarowitz, 2008).

3.4. Micro- and macronutrients

The content of calcium, phosphorus, selenium, iodine, and fluoride are shown in Table 1. All samples with the exception of smoked sprat were prepared from muscles tissue of fish. Therefore, significant content of calcium (on average 559 mg 100 g⁻¹) was found only in smoked sprat. In the remaining products, the levels of this element were low (from 14 mg 100 g⁻¹ in smoked Norwegian salmon to 74 mg 100 g⁻¹ in smoked herring).

### Table 1

<table>
<thead>
<tr>
<th>Nutrient</th>
<th>Sample 1</th>
<th>Sample 2</th>
<th>Sample 3</th>
<th>Sample 4</th>
<th>Sample 5</th>
<th>Sample 6</th>
<th>Sample 7</th>
<th>Sample 8</th>
<th>Sample 9</th>
</tr>
</thead>
<tbody>
<tr>
<td>Protein (g)</td>
<td>19.51</td>
<td>20.01</td>
<td>19.54</td>
<td>22.35</td>
<td>19.71</td>
<td>23.34</td>
<td>12.81</td>
<td>15.43</td>
<td>15.77</td>
</tr>
<tr>
<td>Fat (g)</td>
<td>(0.71)</td>
<td>(2.28)</td>
<td>(0.79)</td>
<td>(2.05)</td>
<td>(1.73)</td>
<td>(0.90)</td>
<td>(1.28)</td>
<td>(1.28)</td>
<td>(1.33)</td>
</tr>
<tr>
<td>Calcium (mg)</td>
<td>46</td>
<td>99</td>
<td>74</td>
<td>14</td>
<td>19</td>
<td>5</td>
<td>4</td>
<td>18</td>
<td>15</td>
</tr>
<tr>
<td>Phosphorus (mg)</td>
<td>207</td>
<td>371</td>
<td>235</td>
<td>229</td>
<td>217</td>
<td>247</td>
<td>87</td>
<td>80</td>
<td>99</td>
</tr>
<tr>
<td>Selenium (µg)</td>
<td>(8)</td>
<td>(45)</td>
<td>(22)</td>
<td>(23)</td>
<td>(13)</td>
<td>(16)</td>
<td>(22)</td>
<td>(19)</td>
<td>(12)</td>
</tr>
<tr>
<td>Fluoride (mg)</td>
<td>(0.11)</td>
<td>0.15</td>
<td>0.46</td>
<td>0.83</td>
<td>1.14</td>
<td>0.98</td>
<td>0.49</td>
<td>0.36</td>
<td>0.11</td>
</tr>
<tr>
<td>Iodine (mg)</td>
<td>0.11</td>
<td>0.15</td>
<td>0.46</td>
<td>0.67</td>
<td>1.00</td>
<td>(0.69)</td>
<td>(0.30)</td>
<td>(0.24)</td>
<td>(0.12)</td>
</tr>
<tr>
<td>Vitamin A₁ (µg)</td>
<td>0.15</td>
<td>0.16</td>
<td>(0.46)</td>
<td>(0.67)</td>
<td>(1.00)</td>
<td>(0.69)</td>
<td>(0.30)</td>
<td>(0.24)</td>
<td>(0.12)</td>
</tr>
<tr>
<td>Vitamin D₃ (µg)</td>
<td>40.2</td>
<td>432</td>
<td>35.2</td>
<td>16.5</td>
<td>17.5</td>
<td>28.0</td>
<td>21.9</td>
<td>32.5</td>
<td>25.9</td>
</tr>
<tr>
<td>Vitamin E (µg)</td>
<td>164</td>
<td>1305</td>
<td>540</td>
<td>1767</td>
<td>2095</td>
<td>1330</td>
<td>569</td>
<td>698</td>
<td>235</td>
</tr>
</tbody>
</table>

*1, 2, 3 - Variety of fish products. 1 - Smoked mackerel; 2 - smoked sprat; 3 - smoked herring; 4 - smoked Baltic salmon; 5 - smoked Norwegian salmon [farmed]; 7 - salted herring fillets; 8 - marinated herring fillets; 9 - fried mackerel in vinegar.*
As our investigation indicated, smoked mackerel, sprat, herring, and Baltic salmon are good sources of selenium, deficiencies of which might be a risk factor for cancer (Smrkolj et al., 2005). The recommended daily allowance of selenium should be met by the consumption of 293 g of smoked mackerel (Table 3).

The products tested were characterized by the very high content of iodine, but the content of fluoride was lower in comparison with that in canned fish (Usydus et al., 2008). The highest levels of iodine (Table 1) were measured in smoked Norwegian salmon (1.14 mg/100 g). The products tested were characterized by the very high content of iodine, but the content of fluoride was lower in comparison with that in canned fish (Usydus et al., 2008). The highest levels of iodine (Table 1) were measured in smoked Norwegian salmon (1.14 mg/100 g). The high levels of iodine were also found in

## Table 2
Composition of fatty acids in the lipids extracted from fish products on Polish market (mean value ± SD).

<table>
<thead>
<tr>
<th>Fatty acids (%)</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
<th>8</th>
<th>9</th>
</tr>
</thead>
<tbody>
<tr>
<td>EPA + DHA</td>
<td>500</td>
<td>1000</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>ALA</td>
<td>142</td>
<td>142</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>LA</td>
<td>52</td>
<td>52</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>DPA</td>
<td>50</td>
<td>50</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>DHA</td>
<td>25</td>
<td>25</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>DPA</td>
<td>50</td>
<td>50</td>
<td></td>
<td></td>
<td></td>
<td></td>
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<td></td>
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</tr>
<tr>
<td>DHA</td>
<td>25</td>
<td>25</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>DPA</td>
<td>50</td>
<td>50</td>
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<td></td>
<td></td>
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<td></td>
<td></td>
</tr>
<tr>
<td>DHA</td>
<td>25</td>
<td>25</td>
<td></td>
<td></td>
<td></td>
<td></td>
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</tr>
</tbody>
</table>

As our investigation indicated, smoked mackerel, sprat, herring, and Baltic salmon are good sources of selenium, deficiencies of which might be a risk factor for cancer (Smrkolj et al., 2005). The recommended daily allowance of selenium should be met by the consumption of 293 g of smoked mackerel (Table 3).

The products tested were characterized by the very high content of iodine, but the content of fluoride was lower in comparison with that in canned fish (Usydus et al., 2008). The highest levels of iodine (Table 1) were measured in smoked Norwegian salmon (1.14 mg/100 g). The high levels of iodine were also found in

## Table 3
Amounts of fish products (g) that contain the recommended amount of particular components.

<table>
<thead>
<tr>
<th>1</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
</tr>
<tr>
<td>3</td>
</tr>
<tr>
<td>4</td>
</tr>
<tr>
<td>5</td>
</tr>
<tr>
<td>6</td>
</tr>
<tr>
<td>7</td>
</tr>
<tr>
<td>8</td>
</tr>
<tr>
<td>9</td>
</tr>
</tbody>
</table>

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salted herring fillets (0.98 mg 100 g⁻¹ on average) and smoked Baltic salmon (0.83 mg 100 g⁻¹ on average). Such high content of iodine in salted products can be due to the fact that iodized salt was used during brining of fish. Significantly lower iodine content (0.03–0.39 mg 100 g⁻¹) was found in canned fish available in Polish market (Usydus et al., 2008).

3.5. Toxic metals

The evaluation of the content of toxic metals in fish products was performed based on the permissible limits set forth in Commission Regulation (EC) no. 1881/2006 of December 2006. In none of the tested samples did the amounts of lead, mercury, or arsenic exceed the permissible limits. In turn, in five samples of smoked sprat, cadmium content exceeded the limits.

The average levels of metals tested were relatively low (with the exception of cadmium content in smoked sprat and herring). With regard to the PTWI (Table 5), it could be assumed that in the presence of cadmium as the contaminant, an adult weighing 70 kg can consume 62.8 kg of smoked trout on a weekly basis, whereas if arsenic is the contaminant, the consumption of only 0.75 kg of smoked mackerel is permitted.

The content of mercury (even under the assumption that total mercury occurs as methylmercury) in samples tested was low and does not diminish the advantageous role of n-3 acids in reducing CHD risk (Yoshizama et al., 2002). Zahir et al. (2005) suggested that persons who routinely consume fish or particular species of fish are at an increased risk of methylmercury poisoning. Fish species containing above 730 µg kg⁻¹ of mercury was classified as species of high risk, whereas species containing below 290 µg kg⁻¹ of mercury was classified as species of medium risk. According to such classification fish products tested in our study belong to medium risk group.

The mercury content measured in our study is significantly lower than that reported by Domingo et al. (2007a) in some fish species destined to Catalonia market in Spain (swordfish – 1930 µg kg⁻¹, red mullet – 230 µg kg⁻¹). In turn, cadmium and lead content were comparable in fish products from Polish and Spain market. Also,

Table 4

<table>
<thead>
<tr>
<th>Substance</th>
<th>Sample 1</th>
<th>Sample 2</th>
<th>Sample 3</th>
<th>Sample 4</th>
<th>Sample 5</th>
<th>Sample 6</th>
<th>Sample 7</th>
<th>Sample 8</th>
<th>Sample 9</th>
<th>Max levels</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mercury (µg)</td>
<td>(10.0)</td>
<td>(9.9)</td>
<td>(27.1)</td>
<td>(19.5)</td>
<td>(10.5)</td>
<td>(14.7)</td>
<td>(16.6)</td>
<td>(24.5)</td>
<td>(19.8)</td>
<td>500</td>
</tr>
<tr>
<td>Cadmium (µg)</td>
<td>(19.2)</td>
<td>42.6</td>
<td>43.0</td>
<td>8.0</td>
<td>8.8</td>
<td>7.8</td>
<td>19.0</td>
<td>9.5</td>
<td>10.5</td>
<td>300</td>
</tr>
<tr>
<td>Lead (µg)</td>
<td>(5.4)</td>
<td>9.5</td>
<td>16.0</td>
<td>2.0</td>
<td>3.1</td>
<td>1.2</td>
<td>19.4</td>
<td>11.3</td>
<td>11.1</td>
<td>300</td>
</tr>
<tr>
<td>Arsenic (µg)</td>
<td>(8.8)</td>
<td>(10.0)</td>
<td>(27.6)</td>
<td>(0.0)</td>
<td>(6.5)</td>
<td>(0.0)</td>
<td>(30.0)</td>
<td>(9.8)</td>
<td>(0.0)</td>
<td>4000</td>
</tr>
<tr>
<td>PCDD/Fs (ng WHO-TEQ)</td>
<td>0.24</td>
<td>3.57</td>
<td>0.66</td>
<td>4.53</td>
<td>0.34</td>
<td>0.12</td>
<td>0.58</td>
<td>1.00</td>
<td>0.41</td>
<td>4.0</td>
</tr>
<tr>
<td>dl-PCB</td>
<td>0.06</td>
<td>4.74</td>
<td>0.78</td>
<td>8.39</td>
<td>1.37</td>
<td>0.46</td>
<td>0.64</td>
<td>1.07</td>
<td>0.96</td>
<td>nd</td>
</tr>
<tr>
<td>PCDD/Fs + dl-PCB (ng WHO-TEQ)</td>
<td>0.84</td>
<td>8.31</td>
<td>1.44</td>
<td>13.12</td>
<td>1.71</td>
<td>0.58</td>
<td>1.22</td>
<td>2.07</td>
<td>1.37</td>
<td>8.0</td>
</tr>
<tr>
<td>PbDEs (ng)</td>
<td>(0.07)</td>
<td>(0.40)</td>
<td>(0.70)</td>
<td>(2.51)</td>
<td>(0.39)</td>
<td>(0.08)</td>
<td>(0.21)</td>
<td>(0.86)</td>
<td>(0.66)</td>
<td>nd</td>
</tr>
<tr>
<td>ΣDDT (µg)</td>
<td>(0.5)</td>
<td>(565)</td>
<td>(1075)</td>
<td>(587)</td>
<td>(720)</td>
<td>(235)</td>
<td>(374)</td>
<td>(985)</td>
<td>(878)</td>
<td>2000</td>
</tr>
<tr>
<td>HCB (µg)</td>
<td>1.26</td>
<td>4.66</td>
<td>0.39</td>
<td>0.85</td>
<td>0.60</td>
<td>0.41</td>
<td>0.57</td>
<td>0.65</td>
<td>0.58</td>
<td>500</td>
</tr>
<tr>
<td>ΣHCH (µg)</td>
<td>0.72</td>
<td>2.24</td>
<td>0.38</td>
<td>1.31</td>
<td>0.55</td>
<td>0.20</td>
<td>0.51</td>
<td>0.50</td>
<td>1.94</td>
<td>nd</td>
</tr>
<tr>
<td>ΣPCB (µg)</td>
<td>12.09</td>
<td>30.89</td>
<td>9.50</td>
<td>42.65</td>
<td>12.55</td>
<td>4.89</td>
<td>7.83</td>
<td>19.17</td>
<td>10.06</td>
<td>75</td>
</tr>
</tbody>
</table>

- nd = Not determined.
- a 1, 2, . . . , 9 = Variety of fish products. 1 – Smoked mackerel; 2 – smoked sprat; 3 – smoked herring; 4 – smoked Baltic salmon; 5 – smoked Norwegian salmon /farmed/; 7 – salted herring fillets; 8 – marinated herring fillets; 9 – fried mackerel in vinegar.
- e WHO-TEQ.
- f Expressed as fat weight basis.

Table 5

<table>
<thead>
<tr>
<th>Substance</th>
<th>Sample 1</th>
<th>Sample 2</th>
<th>Sample 3</th>
<th>Sample 4</th>
<th>Sample 5</th>
<th>Sample 6</th>
<th>Sample 7</th>
<th>Sample 8</th>
<th>Sample 9</th>
<th>PTWI a, b, c</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cadmium (µg)</td>
<td>25520</td>
<td>11502</td>
<td>11395</td>
<td>61250</td>
<td>55682</td>
<td>62820</td>
<td>25789</td>
<td>51579</td>
<td>46667</td>
<td>7 µg kg⁻¹ body weight 490 µg</td>
</tr>
<tr>
<td>Mercury (µg)</td>
<td>2235</td>
<td>4358</td>
<td>1647</td>
<td>1578</td>
<td>2814</td>
<td>2450</td>
<td>2328</td>
<td>2141</td>
<td>2137</td>
<td>1.6 µg kg⁻¹ body weight 112 µg</td>
</tr>
<tr>
<td>Arsenic (µg)</td>
<td>742</td>
<td>879</td>
<td>914</td>
<td>1542</td>
<td>1203</td>
<td>1353</td>
<td>1300</td>
<td>958</td>
<td>829</td>
<td>25 µg kg⁻¹ body weight 1750 µg</td>
</tr>
<tr>
<td>PCDD/PCDF+dl-PCB (ng)</td>
<td>1167</td>
<td>118</td>
<td>680</td>
<td>75</td>
<td>573</td>
<td>1690</td>
<td>803</td>
<td>473</td>
<td>715</td>
<td>14 µg kg⁻¹ body weight 0.98 ng</td>
</tr>
</tbody>
</table>

- a 1, 2, . . . , 9 = Variety of fish products. 1 – Smoked mackerel; 2 – smoked sprat; 3 – smoked herring; 4 – smoked Baltic salmon; 5 – smoked Norwegian salmon /farmed/; 7 – salted herring fillets; 8 – marinated herring fillets; 9 – fried mackerel in vinegar.
- b PTWI – Provisional Tolerable Weekly Intake.
- c In a male adult weighing 70 kg.
commercial fish taken from New Jersey market (Burger and Gochfeld, 2005), and canned fish from Turkish market contained cadmium and lead at levels comparable with that found in fish products from Polish market (Tuzen and Soylak, 2007).

On the basis of current seafood consumption data in Belgium it was concluded that the contamination of seafood with methylmercury did not pose a threat for human health (Sioen et al., 2007). High content of methylmercury was noted only in big predator fish as swordfish and tuna. Therefore it is recommended, especially for pregnant women, to avoid these species in their diet (Sioen et al., 2008).

3.6. Organochlorine pesticides (OCP) and polychlorinated biphenyls (PCBs)

The limits for OCP and indicator PCBs are not establish in Poland, so we have referred our results to the permissible limits binding in some European Union countries. The levels of OCP are compared with limits established in German: HCB 0.5 mg kg⁻¹ fat; α- and β-HCH 0.05 mg kg⁻¹ fat, γ-HCH 2 mg kg⁻¹ fat; ΣDDT 2 mg kg⁻¹ wet weight (FAO, 1989), while levels of sum of seven indicator PCBs are compared with permissible limit: 75 ng g⁻¹ wet weight established in Belgium after the Belgian dioxin crisis in 1999 (Maes et al., 2008). All results presented in Table 4 are expressed on wet weight basis, but in case of HCB and HCHs we have assessed results expressed on fat weight basis (data not shown in the Table 4). Moreover, Table 4 contains concentration of the sum of three HCH isomers, but the concentration of each isomer was referred to the proper limit.

The results presented for contents of OCP (α-, β-, γ-HCH as sum of HCH, HCB, pp'-DDE, pp'-DDD, pp'-DDT as sum of DDT) and PCBs (total of congeners IUPAC nos. 28, 52, 101, 118, 138, 153, 180) in the tested fish products were low relative to the permissible limits. None of the tested samples were found to exceed the permissible limits of OCP/PCB. The highest average contents of ΣDDT, ΣHCH, and ΣPCB (Table 4) were measured in smoked Baltic salmon (50.0 μg kg⁻¹, 1.31 μg kg⁻¹, and 42.65 μg kg⁻¹, respectively) and in smoked sprat (9.71 μg kg⁻¹, 2.24 μg kg⁻¹, and 30.89 μg kg⁻¹, respectively). However, the levels of PCBs noted in products made from these species are low in compare with levels noted for eel. The average concentration of indicator PCBs reported by Maes et al. (2008) in European eel (Anguilla anguilla) captured in Belgium accounted for 605 pg kg⁻¹. The highest content of ΣDDT and ΣPCB in one of the smoked Baltic salmon sample accounted for 3.6% and 88% of permissible limits, respectively. It could be concluded that the levels of OCP and PCBs in tested samples were low in a comparison with the amounts recommended as permissible limits. Our investigation on bioaccumulation of OCP and indicator PCBs in Baltic fish, conducted in 1995–2006 period indicated that levels of these contaminants in fish were also lower than permissible limits quoted in current paper (Szlinder-Richert et al., 2008b,c).

3.7. Polybrominated diphenyl ethers (PBDEs)

The tests of the levels of PBDEs (total of 7 congeners – BDE-28, BDE-47, BDE-100, BDE-99, BDE-154, BDE-153, BDE-183) indicated (Table 4) that the highest average content of these compounds was found in smoked Baltic salmon (3962 ng g⁻¹) and the lowest in smoked trout (691 ng g⁻¹). Since the recommended PTWI (EFSA, 2005; p. 71) is 0.7 μg kg⁻¹ body weight (49000 ng for an adult weighing 70 kg on a weekly basis), this limit is high in comparison with the content of these contaminants measured in the tested products. It was shown that with respect to this limit (Table 5), it is possible to consume more that 12 kg of smoked Baltic salmon and as much as 70 kg of smoked trout without exceeding the PTWI recommended for PBDEs. However it should be stressed that this recommended PTWI is derived from the limited set of data, and there is a note in EFSA Journal (2005; p. 71) that this value is considered as less robust. It should be emphasized that congener BDE-47 accounted for 50% of the amount of all tested congeners. Similar result was obtained by Miyake et al. (2008) who tested fish from Chinese market: BDE-47 was the predominant PBDE congener. This congener is characterized by the most efficient permeation from food. It was estimated that approximately 90% of BDE-47 ingested with food remains in an organism (Winneking, 2002).

The contents of PBDEs in our study are higher than concentrations of total PBDEs found by Domingo et al. (2008) in fish and shellfish (563.9 ng kg⁻¹ of wet weight) from Catalonia market (Spain).

3.8. PCDD/Fs and dl-PCBs

The contents (Table 4) of PCDD/PCDFs and dl-PCBs (a total of 4 congeners of non-ortho PCB – nos. 77, 81, 126, 169 and 8 congeners of mono-ortho PCB – nos. 105, 114, 118, 123, 156, 157, 167, 189), in the tested products given as sum of WHO-TEQs, were compared with permissible values set forth in Council Regulation (EC) No. 199/2006 of February 3, 2006, and with the PTWI for a person weighing 70 kg at 14 pg WHO-TEQ kg⁻¹ of body weight (EFSA, 2005). The content of PCDD/Fs + dl-PCB exceeded the permissible limit (8 pg WHO-TEQ g⁻¹) in smoked sprat and smoked Baltic salmon samples. However, it should be emphasized that the consumption of these products in Poland is very low and the intake of the above-mentioned contaminants with these products on a weekly basis would account for 0.006 and 0.12 pg WHO-TEQ kg⁻¹ of body weight, respectively. However, the ingestion of these products by pregnant/nursing women and young children is not recommended. Data shown in Table 5 indicate that with respect to the PTWI values, the consumption of tested products by a man weighing 70 kg can range between 75 g (smoked Baltic salmon) and 1690 g (smoked trout). As our previous study revealed in a case of canned fish, this amount was 327 g (Usydus et al., 2008). Since average weekly consumption of fish products in Poland is approximately 70 g it seems that currently, fish products tested during our investigation do not pose the threat for the health of Polish consumers in regard to PCDD/F and dl-PCBs content.

According to Sioen et al. (2007), in Belgium, the excess of tolerably intake of dioxin-like compounds via food can occur, in spite of the low consumption of Baltic fish. Domingo and Bocio (2007) reported in their literature review that an average daily intake of PCDD/Fs and dl-PCBs in Finland accounted to 54 pg WHO-TEQ and 41 pg WHO-TEQ, respectively, and the contribution of fish in this intake was 16%. Higher intake was estimated by Bocio et al. (2007) for consumers from Catalonia (Spain). For a standard adult man (70 kg body weight), the intake of PCDD/Fs and dl-PCBs through consumption of fish and other seafood in Catalonia was estimated to be 38.0 pg WHO-TEQ d⁻¹. Tuna, hake and sardine were the species with the highest contribution to this intake.

4. Conclusion

Two conflicting views regarding the importance of fish consumption in the human diet are presented in the world literature. The main themes of the discussion are the benefits for consumer health from the nutritional properties of fish, particularly from constituent n-3 fatty acids, and the risks posed by the contamination of fish with dioxin-like substances and methylmercury.

Recently, other uncertainties concerning the advantageous impact of acids from n-3 family on human health have appeared. The observational studies have generally favored a beneficial role of n-3 fatty acids in the prevention of heart disease, particularly...
in the prevention of sudden cardiac death. However, the results of more recent randomized controlled studies have led to conclusions regarding the benefit more controversial with the suggestion of possible harmful effects arising from fish oil supplementation to those diagnosed with cardiovascular disease (Block and Pearson, 2006). There is little controversy over a positive role of n-3 acids in the prevention of secondary cardiovascular disease (Kris-Ethernton et al., 2003) and in the reduction of blood triglyceride levels (Block and Pearson, 2006) and high blood pressure (Morrisey et al., 1993).

Similarly, as in case of canned fish (Usydus et al., 2008), also in other fish products in Polish market, dioxins and dl-PCBs could pose the most significant threat. The remaining pollutants tested in this study (toxic metals, non-dioxin like PCBs, OCP, and PBDE) are not much important, taking into account the present fish consumption in Poland (Table 5). The highest levels of PCDD/Fs and dl-PCBs were observed in smoked Baltic salmon and smoked sprat, and these products should be avoided by pregnant/nursing women and young children. It is very difficult to resolve the nutritional-toxicological conflict regarding seafood. Some authors (Cohen et al., 2005; Mozaffarian and Rimm, 2006), conclude that the benefits of fish consumption outweigh the potential risk, but other researchers disagree with such conclusion. On the basis of a wide literature study, Stern (2007) demonstrated that the health benefits in lowering the risk of cardiovascular disease stemming from high PUFA intake from fish are diminished by elevated risk connected with the presence of the excessive amount of methylmercury in fish. Similarly, Domingo et al. (2007a) even though they did not dispute the high importance of fish consumption for the reducing of the risk of cardiovascular disease, they pointed at a presence of persistent organic pollutants, methylmercury and other contaminants in fish as a serious health problem connected with fish consumption.

The important conclusion stemming from the study on benefits and risk related to fish consumption is that species and quantity of fish consumed is of significance importance for consumer health. As Stern (2007) concluded, consumers should make a wisdom choice from fish and fish products available in market, to maximize benefits (high PUFA content) and minimize risk (low contaminants content).

Acknowledgments

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