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Marine and farmed fish on the Polish market: Comparison of the nutritive value and human exposure to PCDD/Fs and other contaminants

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ABSTRACT

Chemical analyses were performed in nine fish species that are popular on the Polish market. These included Baltic fish (cod, herring, salmon), fish farmed in Poland (carp, trout), marine fish imported from China (Alaska pollock, sole), and farmed fish imported from Vietnam and China (sutchi catfish, tilapia). The nutritional composition (amino acid, micro- and macronutrients, fat-soluble vitamins – A_1, D_3, E) and certain contaminants (organochlorine pesticides, OCPs; indicator polychlorinated biphenyl, PCB_6; polychlorinated dibenzo-paradioxins and polychlorinated dibenzofurans, PCDD/Fs; dioxin-like polychlorinated biphenyls, dl-PCBs; organotin compounds, OCTs; dyes, malachite green and crystal violet; veterinary drug residues, nitrofurans and chloramphenicol; toxic metals, Cd, Pb, Hg) in the muscle tissues of fish were determined. It was confirmed that the fish species analyzed were excellent sources of amino acids, and were rich in phosphorous and selenium. Baltic Sea fish (salmon, herring), fish farmed in Poland (carp and trout), and tilapia were also rich in vitamin D_3.

Traces of OCP, PCB_6, OCT, dyes, veterinary drug residues, and heavy metals were detected in concentrations which do not pose a threat to consumers at the current rate of fish consumption in Poland. However, the problem might arise from the content of PCDD/Fs and dl-PCBs in fatty Baltic fish. The fish species analyzed, differed in their nutritional values and degrees of contamination. We suggest that for optimum health and safety, it is advisable that consumers include a variety of different fish species in their diets.

1. Introduction

In today's society there is a growing interest in nutrition as a way to ensure good health. Improper nutrition is linked to increased incidence of diseases of civilization including circulatory disorders, cancer, diabetes, tooth decay, obesity, and constipation. Food products that are advantageous for human health include, among others, fish and fish products. The most beneficial components for human health that occur in fatty fish and fish products are n-3 polyunsaturated fatty acids (PUFA), particulary eicosapentaenoic acid (EPA), and docosahexaenoic (DHA) (Berbert et al., 2005; Calo et al., 2005; Norat et al., 2005; Wolk et al., 2006). Discussions of the health benefits of fish consumption focus to a lesser extent on nutritional components such as digestible proteins rich in essential amino acids, fat-soluble vitamins (especially vitamin D_3), micro- and macroelements such as calcium, magnesium, iodine, and selenium. These nutrients are important to the health and proper functioning of the human body. Since they occur in fish in higher quantities than in other popular food products, fish consumption is a good way to supplement the overall diet.

Addition to nutrients that are beneficial to human health, fish also contain undesirable substances. The conclusion of many publications, especially those by nutritionists, affirm that benefits of fish consumption are greater than any of the potential risks (Cohen et al., 2005; Mozaffarian and Rimm, 2006). Some authors, however, disagree. Based on a extensive literature review, Stern (2007) reports that the effectiveness of ingesting EPA and DHA from fish sources to reduce the incidence of cardiovascular diseases, might be lowered because of the growing risks linked to the excessive methylmercury (MeHg) content of fish. Domingo et al. (2007) recognizes the beneficial role of fish consumption in lowering the risk of circulatory diseases, but they conclude that the presence of persistent organic compounds, MeHg, and other pollutants in fish pose significant health risks.

Recently in the Polish, European, and American markets many new farmed fish species (Vietnam, China), and fish from tropical or temperate oceanic regions, African rivers and lakes have appeared (Getabu et al., 2003; Tucker, 2003). These new fish on the market prompted the undertaking of the current study to compare the nutritional value and degree of contamination of these new fish species with Baltic and farmed fish that are popular among Polish

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consumers. The authors' previous article (Usydus et al., 2011) reported an in-depth evaluation of the nutritional values of the analyzed fish species in reference to the fatty acid content of their muscle tissues. In the current study analyses of amino acids, micro- and macroelement content, fat-soluble vitamins, and in addition, certain inorganic and organic contaminants in the muscle tissues of the same fish species are presented.

2. Materials and methods

2.1. Study material

The concentration of minerals, fat-soluble vitamins, protein, amino acid and certain, undesirable substances of the muscle tissues of nine fish species were determined. The following fish were analyzed:

a. Baltic fish caught in the Polish catch area:
   - cod (*Gadus* morhua callarias);
   - herring (*Clupea* harengus membras);
   - Baltic salmon (*Salmo salar*);
b. fish farmed in Poland:
   - carp (*Cyprinus carpio*);
   - rainbow trout (*Oncorhynchus mykiss*);
c. marine fish imported from China:
   - Alaska pollock (*Theragra chalcogramma*) from fishing areas FAO 61 and FAO 67 in the Pacific;
   - sole (*Limanda aspera*) from fishing area FAO 67, in the Pacific
d. farmed fish imported from Vietnam and China:
   - sutchi catfish (*Pangasius hypophthalmus*) farmed in Vietnam;
   - tilapia (*Oreochromis niloticus*) farmed in China.

Ten batches of fish from each of the species, which constituted separate samples, were collected and analyzed. The Baltic fish were obtained in 2008 and 2009, during scheduled cruises of the r/v Baltica (cod and herring) or from fishing cutters (salmon) operating in the Polish catch area. The imported fish, which were frozen, skinned fillets in 0.5 kg packages, were purchased at supermarkets during 2009. Sampling was carried out in such a way that each sample was characterized by a different date of production. Fish farmed in Poland were purchased fresh from either supermarkets or directly from the fish farms.

The fish obtained during cruises of the r/v Baltica (cod, herring) were hermetically sealed and then stored in the ship's freezer at a temperature of −18 °C, during 2 weeks.

2.2. Sample preparation

The frozen fish (cod, herring, imported fish) were defrosted for 16 h at a temperature of 2–4 °C in a refrigerator. The liquid released during defrosting was discarded. The loss of amino acid and soluble proteins during defrosting was neglected. The whole fish or fillets were then dried off with paper towels. The defrosted fish and fresh fish were filleted and skinned. These fillets and fillets of imported fish were homogenized in a mixer (Multi Processor, Zelmer) for about 60 s at 1300 revolutions per minute. Each sample comprised about 1 kg of fish muscle tissue. The fish samples which were used to determine the fat-soluble vitamins, persistent organic compounds, and veterinary medicines were freeze-dried in an Alpha 2–4 LSC freeze dryer (Christ, GmbH, Osterode am Harz, Germany).

Analyses of protein amino acid composition, traces of PCDD/F, dl-PCB, OCT, dyes, and veterinary drugs were preformed in two replicates on pooled samples. These average samples were obtained by mixing equal amounts of ten different samples of the same fish species. Analyses of fat-soluble vitamins, minerals, toxic metals, OCP, and ΣPCB_6 were performed on ten different samples from the same fish species.

2.3. Analytical methods

Amino acids: The determinations of amino acids were conducted at the Central Laboratory of the National Research Institute of Animal Production in Krakow, Poland. Amino acids in the freeze-dried samples were analyzed after acid hydrolysis in 6 N HCl for 22 h, at 110 °C in glass tubes under nitrogen. Cystine and methionine were determined as cysteic acid and methionine sulphone, respectively, by performic acid oxidation before their digestion, using 6 N HCl (Moore, 1963; Blackburn, 1968). Tryptophan was determined by the method of Landry et al. (1992), after the alkaline hydrolysis of each sample. Chromatographic analysis was conducted with a Beckman-System Gold-126 AA, equipped with an ion-exchange column and an UV–VIS detector, after post-column derivatization with ninhydrin. All analyses were performed in duplicate for each sample, and the results in Table 1 are summarized as an average of two determinations. Quantitation of each amino acid was based on external standards.

Mineral composition: Mineral analyses were conducted the laboratory of the Sea Fisheries Institute in Gdynia, Poland. The following micro and macronutrients (calcium – Ca, phosphorous – P, magnesium – Mg zinc – Zn, copper – Cu, selenium – Se) and toxic metals (mercury – Hg, cadmium – Cd, lead – Pb) were determined. The analyses were performed according to the methods described in our previous paper (Usydus et al., 2009). Briefly, samples for testing the contents of most of the minerals were wet degested with concentrated nitric acid in MD-2100 microwave oven. 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. The measurement series were preceded by measuring the mercury concentration in reference material – SRM 1566b (oyster tissue).

Fat-soluble vitamins (A_1 – all-trans-retinol, D_3 – cholecalciferol, E – α-tocopherol): Were determined in the laboratory of the Sea Fisheries Institute in Gdynia according to the method described in Usydus et al. (2009). Briefly, freeze-dried samples were saponificated, and vitamins were extracted with hexane. Extracts were evaporated, and the residue was dissolved in methanol. Final determinations were performed with the HPLC technique. Vitamins A_1 and E were determined by fluorescence and vitamin D_3 with a UV detector. The quantitation of vitamins A_1 and E was performed based on the area of standard peaks, while vitamin D_3 was determined using vitamin D_2 as the internal standard. The internal standard was added to samples prior to saponification.

Organochlorine pesticides (hexachlorocyclohexane isomers – α-, β-, γ-HCH; hexachlorobenzene – HCB; 1,1,1-trichloro-2,2-bis(4-cholor ophenyl) ethane – pp′-DDT and DDT metabolites, 1,1,-dichloro-2,2-bis(4-chlorophenyl)ethane – pp′-DDD; 1,1,-dichloro-2,2-bis(4-chlorophenyl) ethylene – pp′-DDE) and six marker polychlorinated biphenyls – PCB_6 (IUPAC nos. 28, 52, 101, 138, 153 and 180) were determined in the laboratory of the Sea Fisheries Institute in Gdynia according to the method described in Usydus et al. (2009). Freeze-dried samples were extracted with *n*-hexane in a Soxtec Avanti apparatus (FOSS) for 4 h. An aliquot of lipid (0.5 g of oil) was dissolved in *n*-hexane in stoppered glass tubes and treated with a mixture of concentrated sulfuric acid and 30% fuming sulfuric acid at a ratio 1:1 v/v. It was shaken periodically for 3 h. After centrifugation