DETERMINATION OF HEAVY METALS IN FISH PRODUCTS

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Abstract: Cadmium, lead and mercury contents in fish were studied. Fresh and frozen fish from 17 FAO localities were bought in Czech markets. Atomic absorption spectrometry technique was used for determination of cadmium, lead and mercury concentration. Ten samples exceeded the maximum permissible limit for mercury (0.5 mg/kg or 1 mg/kg for selected fish species) and three fish samples exceeded the maximum limit for cadmium (0.05 mg/kg) set by Commission Regulation (EU) No1881/2006. The limit of lead concentration (0.3 mg/kg) was not exceeded in any fish sample. This study shows that fish samples of marlin (Tetrapturus albidus) and swordfish (Xiphias gladius) are one of the most contaminated fish which can pose a great risk for human health after consumption. Because mercury and cadmium contents in some samples were higher than maximum limits recommended by FAO/WHO, our research led to withdraw of some batches of the fish from the Czech markets.

Key Words: mercury, cadmium, lead, fish

INTRODUCTION

Heavy metals such as cadmium, lead and mercury are significant environmental contaminants. In the Czech Republic, as in other developed parts of the world, there is an increased risk of heavy metals (Hg, Cd, Pb etc.) in the environment. Currently, the heavy metal compounds released into the aquatic ecosystem mainly from anthropogenic sources, i.e. as a result of industrial, agricultural and mining activities (CCME 2000, Stancheva et al. 2013). The contamination of the environment by heavy metals reduces the hygienic quality of foodstuffs (freshwater and especially marine species of fish) obtained from aquatic organisms (Atobatele 2014).

Maximum levels for cadmium, lead and mercury in foodstuffs are in the Czech Republic set by the framework EU legislation, namely by the Commission Regulation No1881/2006. A tolerable Weekly Intake (TWI) established by the international scientific committee FAO/WHO for mercury, cadmium, and lead is 1.3 μg/kg Hg body weight (b. w.), 7 μg/kg Cd b. w. and 25 μg/kg Pb b. w., respectively (Commission Regulation No1881/2006).

Because a healthy lifestyle and unconventional food is currently interesting for many people, a lot of specialty stores devoted to the sale of seafood are established in landlocked states. The same situation can be observed in the Czech Republic. In recent years, there is an expansion of shops selling fresh seafood. This led us to monitoring of the trade network in the Czech Republic, and particularly to assess of the risks associated with the consumption of contaminated fish.

MATERIAL AND METHODS

Collection of samples

From September 2015 to June 2016 33 species of fish samples from 17 FAO localities were purchased in Brno City (Czech Republic) markets. A minimum of three samples per batch were
purchased. Total amount of bought and analysed fish samples was 159, contaminated fish species were purchased several times from the other batches for monitoring of contamination. Samples were transported to the laboratory and stored in -20 °C until the time of analysis. Frozen samples were slowly thawed and 0.1–0.6 g were weighed for individual analysis. Analysed fish species are presented in Table 1.

Table 1 Overview of fish species subjected to analysis

<table>
<thead>
<tr>
<th>English name</th>
<th>Latin name</th>
<th>English name</th>
<th>Latin name</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alaska Pollock</td>
<td>Theragra chalcogramma</td>
<td>Golden redfish</td>
<td>Sebastes marinus</td>
</tr>
<tr>
<td>Angler</td>
<td>Lophius piscatorius</td>
<td>Greater argentine</td>
<td>Argentina silus</td>
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<tr>
<td>Argentine hake</td>
<td>Merluccius hubbsi</td>
<td>Greenland halibut</td>
<td>Reinhardtius hippoglossoides</td>
</tr>
<tr>
<td>Asian sea bass</td>
<td>Lates calcarifer</td>
<td>Indo-Pacific sailfish</td>
<td>Istiophorus platypterus</td>
</tr>
<tr>
<td>Atlantic herring</td>
<td>Clupea harengus</td>
<td>Nile perch</td>
<td>Lates niloticus</td>
</tr>
<tr>
<td>Atlantic mackerel</td>
<td>Scomber scombrus</td>
<td>Nile tilapia</td>
<td>Oreochromis niloticus</td>
</tr>
<tr>
<td>Atlantic salmon</td>
<td>Salmo salar</td>
<td>Pink salmon</td>
<td>Oncorhynchus sgorbuscha</td>
</tr>
<tr>
<td>Blue shark</td>
<td>Prionace glauca</td>
<td>Ray</td>
<td>Raja</td>
</tr>
<tr>
<td>Bogue</td>
<td>Boops boops</td>
<td>Red mullet</td>
<td>Mullus barbatus</td>
</tr>
<tr>
<td>Dusky grouper</td>
<td>Epinephelus marginatus</td>
<td>Salmon trout</td>
<td>Oncorhynchus mykiss</td>
</tr>
<tr>
<td>Escolar</td>
<td>Lepidocybium flavobrunneum</td>
<td>Senegalese hake</td>
<td>Merluccius senegalensis</td>
</tr>
<tr>
<td>European anchovy</td>
<td>Engraulis encrasicolor</td>
<td>South Pacific hake</td>
<td>Merluccius Gayi</td>
</tr>
<tr>
<td>European pilchard</td>
<td>Sardina pilchardus</td>
<td>Swordfish</td>
<td>Xiphias gladius</td>
</tr>
<tr>
<td>European seabass</td>
<td>Dicentrarchus labrax</td>
<td>Tub gurnard</td>
<td>Trigla lucerna</td>
</tr>
<tr>
<td>Flatfish</td>
<td>Pleuronectiformes</td>
<td>White marlin</td>
<td>Tetraprurus albidus</td>
</tr>
<tr>
<td>Flathead grey mullet</td>
<td>Mugil cephalus</td>
<td>Yellowfin tuna</td>
<td>Thunnus albacares</td>
</tr>
<tr>
<td>Gilthead bream</td>
<td>Sparus aurata</td>
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</tr>
</tbody>
</table>

Determination of cadmium and lead in fish samples

A microwave digestion (Ethos ONE, Milestone, Italy) was used for decomposition of fish samples. The 10 ml HNO₃ (1 : 1) was added to 600 ± 0.1 mg of fresh fish muscle tissue and it was decomposed in the microwave oven at 210 °C (1000 W) for 30 min.

Electrothermal atomic absorption spectrometer (Series AA 280, Agilent Technologies, United States, equipped with Zeeman correction) was used under the optimized conditions for determination of Cd (228.8 nm) and Pb (283.3 nm) in mineralized fish samples. The standards 1 g/l of Cd and Pb (Merck, Germany) were used for calibration. Temperature of pyrolysis was 500 °C for Cd and 1000 °C for Pb, atomisation temperature was 1800 °C for Cd and 2100 °C for Pb. Pd/Mg(NO₃)₂ was used as modifier. The limits of detection (LOD) for cadmium and lead determination were 0.12 and 3.11 µg/kg, respectively.

Determination of total mercury content in fish samples

An AMA 254 advanced mercury analyzer (Altec, Prague, Czech Republic) was used for the determination of total Hg concentration by direct analysis of fish samples. 0.1 g of fish sample was inserted into pre-cleaned combustion boats and loaded into the AMA 254 analyser. During analysis the sample was dried at 120 °C for 90 s and thermally decomposed at 550 °C for 180 s under an oxygen flow. Selectively trapped mercury was subsequently released from the gold amalgamator by a brief heat-up and finally quantified (measuring cycle, 60 s) as Hg⁰ by the cold-vapor AAS technique at 253.65 nm. The limit of detection (LOD) for mercury determination was 0.1 µg/kg.

RESULTS AND DISCUSSION

Content of cadmium in fish samples

Cadmium concentration in analysed fish muscle tissues and cadmium limits (Commission Regulation (EU) No1881/2006) are shown in Figure 1. Three limits for cadmium are highlighted in this
figure for defined fish species. Limit 0.3 mg/kg is set only for swordfish, limit 0.1 mg/kg is for 11 selected fish species according to this Regulation and limit 0.05 mg/kg is set for all other fish species.

**Figure 1 Cadmium content in fish samples**

![Cadmium concentration graph](image)

Cadmium was detected only in the samples mentioned in Figure 1. The cadmium concentration in the other fish samples was below LOD (0.12 µg/kg). The highest concentration of cadmium (0.1809 ± 0.0362 mg/kg) was determined in the muscle tissue of white marlin (*Tetrapturus albidus*).

Only three fish samples exceeded the cadmium limit – tub gurnard (0.0950 ± 0.0047 mg/kg), ray (0.1203 ± 0.0060 mg/kg) and white marlin (0.1809 ± 0.0362 mg/kg). After repeated purchase of fish, the limit was not exceeded as is shown in Figure 1 (Ray II, Tub gurnard II and III). According to the international scientific committee FAO/WHO calculation of risk for human health, 70 kg man can eat 27 portions (100 g) of analysed white marlin for reaching cadmium Tolerable Weekly Intake (TWI).

Jinadasa et al. (2014) determined the highest cadmium content in swordfish (0.087 mg/kg), which belongs to a group of billfish (together with marlin and sailfish) (Rodrigues and Amorim 2016). Although Indo-Pacific sailfish (*Istiophorus platypterus*) belongs to billfish, but there we didn't detect an over limit content of cadmium in our samples. The same situation was observed in the case of mercury content in Indo-pacific sailfish.

**Content of lead in fish samples**

The concentration of lead in analysed fish samples was very low (see Figure 2). The highest concentration of lead (0.0250 ± 0.0013 mg/kg) was determined in the muscle tissue of swordfish (*Xiphias gladius*). 70 kg man can eat 700 portions (100 g) of analysed swordfish for reaching lead Tolerable Weekly Intake (TWI). Only samples with lead concentration higher than LOD (3.11 µg/kg) are presented in Figure 2.

Fish species showed lower lead contents compared to Cd and total Hg. Zaza et al. (2015) reported higher lead content in the European seabass (0.1670 ± 0.0580 mg/kg), but in our samples of this fish, concentration of lead was below LOD. Squadrone et al. (2016) reached the same findings as we obtained.
Content of mercury in fish samples

The Figure 3 shows the total mercury concentrations in muscle tissue of analysed fish samples.

Mercury was detected in all analysed fish samples. Only samples with mercury content higher than 0.15 mg/kg are presented in Figure 2. The highest concentration of the mercury (10.42 ± 2.08 mg/kg) was determined in the muscle tissue of white marlin (Tetrapturus albidus), while the lowest concentration (0.0031 ± 0.0002 mg/kg) was determined in Nile tilapia (Oreochromis niloticus). TWI is reached by eating of only 0.09 portion (the portion is 100 g) of analysed white marlin by 70 kg man. This is only 9 g of the fish weekly.
Ten fish samples exceeded the maximum permissible limit for mercury set by Commission Regulation (EU) No1881/2006. The sample of dusky grouper (*Epinephelus marginatus*) exceeded the lower mercury limit (0.5 mg/kg), while the higher limit for selected fish species (1.0 mg/kg) was exceeded in the case of swordfish (*Xiphias gladius*), blue shark (*Prionace glauca*) and white marlin (*Tetrapturus albidus*). Bergés-Tiznado et al. (2015) reported similar results (0.5600 ± 0.0400 mg Hg/kg) for sailfish.

Rodriques and Amorim (2016) published a review about mercury levels in marlin and swordfish. In this review, Shomura and Craig (1972) presented that the highest content of mercury were found in marlin, specifically from the area of Hawaii, which belongs to the fishing area FAO 77 (Pacific, Eastern Central). Our samples of marlin came from the fishing area FAO 87 (Pacific, Southeast) which is in close proximity to FAO 77.

**CONCLUSION**

As a consequence of shops selling fresh seafood expansion, the ordinary consumers can easily buy unusual fish species (for our geographical area) and they are often unaware of the risks associated with consumption of these fish. Therefore thorough monitoring of heavy metals concentrations in fish which are imported from abroad and are widely available on the market of landlocked countries is necessary.

Since 2004, the European system RASFF (Rapid Alert System for Food and Feed) has recorded in the Czech Republic 14 cases of above-limit content of heavy metals in fish where six cases were related to Hg, six cases to Cd and two cases to both elements. Two reports have already been submitted by the Czech Republic in 2016. Our research has led to reporting of 8 cases of above-limit content of heavy metals in fish, which were submitted into the European system RASFF The last case which we reported was over the limit of cadmium content in swordfish submitted in February 2016, which was followed by the withdrawal from the markets in EU.

As our study confirmed, predatory fish species (such as marlin, shark or swordfish), which are on the top of the food chain, pose a greater risk for consumer due to the cumulative property of heavy metals in organisms.

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