Toxic metal contamination and total organic carbon content in the meat of the main fish species imported and sold in Romanian's supermarkets

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Abstract

In Romania as in Western Europe in the last years a mass panic installed among the consumers of cheap fish meat imported mostly from Vietnam – *Pangasianodon hypophthalmus* (S 1878). This problem was intensively fuelled by mass media and different movies uploaded on internet. The metal compounds, once released in the environment, can easily contaminate the food webs and finally the body of the highest rank consumers. The toxic metals in high concentrations are damaging the biological functions and in the end they may trigger the death of the organism (depending on the concentration and the body weight). These metals cannot be biodegraded in the environment; they are quickly transferred from the environment and accumulated in the biological tissues. This study investigated the level of arsenic, mercury, lead and cadmium in the meat of *Pangasianodon hypophthalmus, Merluccius hubbsi, Scomber scombrus*, from nine different brands using HR-CS GF-AAS and HG-AAS techniques.

Keywords: Toxic metals, Total organic carbon, HR-CS GF-AAS, HG-AAS

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Introduction

Food resource contamination with various toxic compounds is an actual problem for the entire human society (Chaid *et al*., 2014; Yildirim *et al*., 2009; Manthey-Karl *et al*., 2016; Guimarães *et al*., 2016; Vilavert *et al*., 2017; Perugini *et al.*, 2014; Madrid et al., 2016; Plavan *et al*., 2017; Strybgary *et al.*, 2015), being associated with severe health problems and death. Fish meat is one of the cheapest animal proteins that can be found on market in high amounts. There are two types of fish resources from where the consumer can chose to buy: fish produced by aquaculture industry and wild captured fish. Both of these resources are under high anthropogenic pressure. For instance, the aquaculture industry is involving a series of chemicals harmful for human health (aquatic pollutants, antibiotics, hormones and artificial fish food). The environmental pollution and the industrial fishing that damage the aquatic ecosystems are playing the major role in case of the wild fish resource. The meat of panga fish became popular among the consumer thanks to its low price, texture, no smell and merchandising form into filets with no skin and spine (Ruiz-de-Cenzano *et al*., 2013, Ionescu *et al*., 2016). In most of the cases, the regular consumer is influenced by the product price and not by quality. Panga fish meat requires high industrial processing techniques (Orban *et al*., 2008) compared with wild captured fish like *Merluccius hubbsi* (Marini, 1933) and *Scomber scombrus* (Linnaeus, 1758). The toxic metals resulted from anthropogenic activities can damage the terrestrial and aquatic biota because they are accumulating very fast, they are toxic and they are not biodegradable (Ionescu *et al*., 2016; Caunii *et al*., 2015; Micu *et al*., 2016). The development of analytical methods, and technology significantly improved the quality and speed of detection for toxic contaminants in food. Mercury, arsenic, cadmium and lead are the most toxic metals that can threat the human population if occur in high amounts.

In this study we investigated the traces of mercury, arsenic, cadmium and lead in meat of *Pangasianodon hypophthalmus* (panga fish), *Scomber scombrus* (Atlantic mackerel) and *Merluccius hubbsi* (Argentine hake) from nine brands with different origins, common in the Romanian supermarkets, using the methods HR-CS GF-AAS and HG-AAS. Total organic carbon content was measured for each brand, this being related to the fish meat quality.

Experimental part

The fish was purchased from three different supermarkets located in the City of Iasi, Romania. These are the largest from this city and belong to same franchise that has same supermarket brand all around Romania. Because of the globalization same product that belongs to a brand can be found everywhere. Each supermarket may have different providers for the same product. In this study it was purchased from each supermarket once per month from February to April a bag of frozen fish or 1 kg self-weighting bag for each studied species: *Pangasianodon hypophthalmus*, *Merluccius hubbsi* and *Scomber scombrus*. These products are the cheapest fish from the market. In the supermarkets we found for same species different brands. The panga fish was found only in industrial processed frozen fillets. Atlantic mackerel and Argentine hake were originated from captured oceanic fish and they were commercialized frozen with or without guts.

Sample preparation

The samples were transported in laboratory and prepared according to the following protocol: fish purchased every month was unfrosted and the water excess was removed using clean paper towels; from each brand it was sampled with PE tools a mas of 10 g of muscle per sample (in triplicates n=3) that was well homogenized in an agate mortar with pestle; from this homogenate was weighted a mas of 1 g in triplicates that were inserted in TFM vessels and mixed for digestion with nitric acid (4 mL, 65% Suprapur Merck) and hydrogen peroxide (1 mL, Merck) (Plavan *et al*., 2017; Strungaru *et al*., 2015) after 25 minutes of reaction the vessels were inserted in Speedwave MWS-2 produced by Berghof using a specific program (Plavan *et al*., 2017; Strungaru *et al*., 2015); the resulted liquid samples were transferred into 50 mL volumetric flasks (Brand) and diluted with ultrapure water produced from double distilled water; for calibration were used certified standard solutions from Merck for arsenic (As), mercury (Hg), lead (Pb) and cadmium (Cd) with each concentration of 1000 mg L-1; mercury was measured with cold vapour hydride generator coupled to AAS that required a sodium borohydride solution and hydrochloric acid (3M, Merck). For the total organic carbon measurements the meat homogenate was dried at 75°C and grinded again to a fine powder. This was analysed in triplicates for each sample, using the direct combustion at 1300°C in solid module coupled to Focus Radiation NDIR detector, multi N/C 2100S produced by AnalytikJena Germany.

Validation of method and results

A total number of 243 samples were prepared and analysed in this study for the metals content. We used fish muscle dry powder certified by European Reference Material ERM-BB422 from Joint Research Centre Institute for Reference Materials and Measurements to validate the method optimization and the results. We prepared 6 samples from this material by weighting a mass of 0.3 g that followed same protocol as a normal sample. Arsenic, cadmium and lead were measured with HR-CS GF-AAS model ContrAA 600 produced by AnalytikJena Germany, which was optimized for this sample matrix. Mercury was measured with cold vapour hydride generator coupled to AAS model Avanta produced by GBC Australia. Argon 5.0 (99.99%) was used

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as carrier gas. The results for validation obtained after the analysis of the reference material were: As – certified value of 12.7±0.7 µg g^{-1} and obtained value of 11.5±0.5 µg g^{-1}; Hg - certified value of 0.601±0.03 µg g^{-1} and obtained value of 0.65±0.4 µg g^{-1}; Cd – certified value of 0.0075±0.0018 µg g^{-1} and obtained value of 0.0081±0.0012 µg g^{-1}; Pb – was not presented in standard certificate and for our method was below LOD.

Statistical analysis

Shapiro-Wilk normality test was performed for the data sets. One-way ANOVA followed by the Tukey HSD test was conducted to demonstrate the significant variance of toxic metal between the brands and fish species (Plavan *et al*., 2017; Strungaru, 2015). All the statistical analyses were carried with OriginPro v.9.3 (2016) software created by OriginLab Corporation, USA.

Results and discussion

In Figure 1 are presented the values of arsenic reported as average±95% confidence for each brand and species. There were significant differences between the brands for same species. There were not observed significant differences between the species regarding the concentration of this element (p>0.05). Panga fish had significant variation between brands (*p<0.05), with the highest values for Brand_2 but with no significant differences compared with other species. The confidence interval is very large suggesting that not all the fishes are originated from same aquaculture system. The concentrations were: Brand_1 with 1.38±1.79 µg g^{-1}, Brand_2 with 2.33±2.98 µg g^{-1} and Brand_3 with 1.55±2.01 µg g^{-1}.

The Argentine hake had significant variations between the brands (*p<0.05) with large confidence intervals of values suggesting that they may be mixed with fish from different catchment areas exposed to pollution sources, possible close to the shore. The concentrations were: Brand_4 with 2.17±2.95 µg g^{-1}, Brand_5 with 2.2±2.86 µg g^{-1} and Brand_6 with 1.32±1.87 µg g^{-1}. For the Atlantic mackerel no differences between brands were observed (p>0.05). The concentrations were: Brand_7 with 2.01±2.55 µg g^{-1}, Brand_8 with 1.91±2.47 µg g^{-1} and Brand_9 with 1.73±2.58 µg g^{-1}. The general concentrations expressed as average±SD for each studied species for arsenic were: panga fish 1.79±0.61 µg g^{-1}, Argentine hake 1.91±0.67 µg g^{-1} and Atlantic mackerel 1.88±0.53 µg g^{-1}. This element is not included in (EC) No 1881/2006 EU legislation that is setting maximum levels for certain contaminants in foodstuffs. In this case was not proved if the concentrations of this element exceeded the maximum permitted values.

Mercury had no significant variance between the brands grouped for each species.

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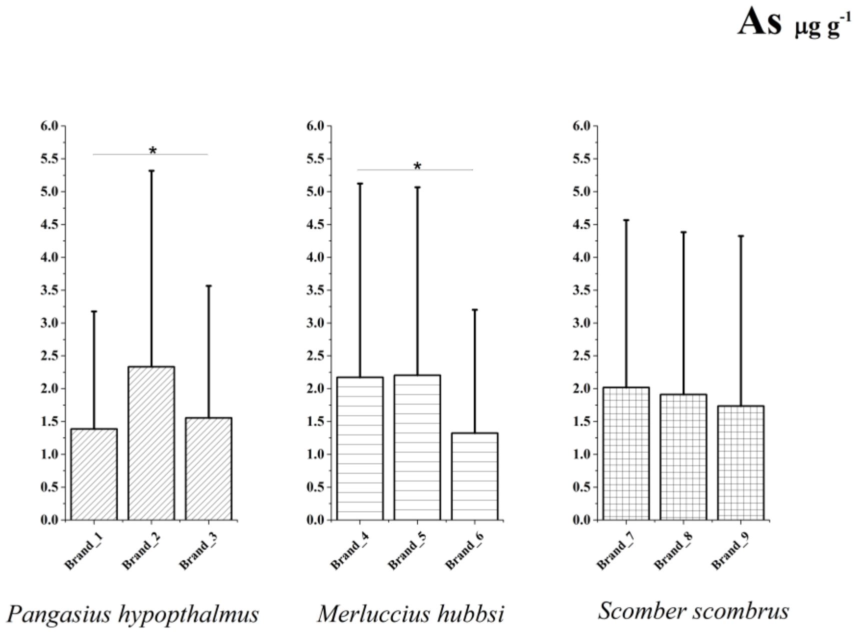

Figure 1: Concentrations of As from each studied brand and species, reported as average±95% confidence with the measurement unit expressed as µg g^{-1} wet weight. The species with significant variance for the one-way ANOVA are marked with line and *-*p*<0.05.

There were significant differences (*$p<0.05$), instead, between panga fish and the wild species captured (Fig. 2).

Panga fish had no significant differences ($p>0.05$) between brands, with the values: Brand_1 with 0.27±0.34 µg g^{-1}, Brand_2 with 0.22±0.28 µg g^{-1} and Brand_3 with 0.25±0.33 µg g^{-1}. Similar to arsenic, the confidence interval is large. Argentine hake had no significant differences ($p>0.05$) between brands, with the values: Brand_4 with 0.14±0.19 µg g^{-1}, Brand_5 with 0.19±0.22 µg g^{-1} and Brand_6 with 0.17±0.30 µg g^{-1}. Same differences were for Atlantic mackerel: Brand_7 with 0.32±0.32 µg g^{-1}, Brand_8 with 0.17±0.23µg g^{-1} and Brand_9 with 0.17±0.23 µg g^{-1}. The general comparisons between the species provide significant results (*$p<0.05$). The highest concentration of total mercury was measured in panga fish: 0.25±0.06 µg g^{-1} (average±SD) that was significant higher than in Argentine hake with 0.17±0.06 µg g^{-1} and Atlantic mackerel with 0.19±0.06 µg g^{-1}. This element is included in (EC) No 1881/2006 with the maximum value of 0.50 µg g^{-1} (mg kg^{-1}) allowed for fishery products and fish muscle. The panga fish did not exceed the limit level for mercury in average but for some samples the levels are at the maximum accepted limit. There were doubts about the quality of the meat according to this element. No significance difference between the two wild species originated from oceanic capture was observed.

The concentrations for cadmium and lead with very low traces were measured in the domain of nanograms. For cadmium and lead were not recorded significant differences between the brands grouped for same species ($p>0.05$).

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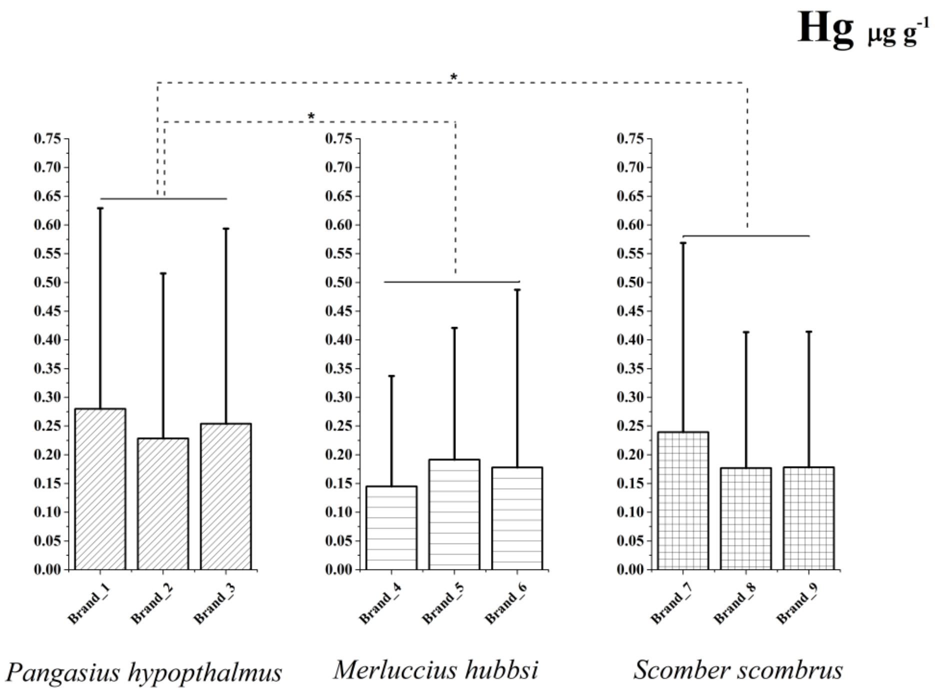

Figure 2: Concentrations of Hg from each studied brand and species, reported as average±95% confidence with the measurement unit expressed as μg g^{-1} wet weight. The comparisons between species with significant variance for Tukey test are marked with *-*p*<0.05.

Differences were observed, instead, between panga fish, Argentine hake and Atlantic mackerel in the case of cadmium (Fig. 3).

The values for cadmium reported as average±95% confidence were: Brand_1 with 0.34±0.62 ng g^{-1}, Brand_2 with 0.27±0.44 ng g^{-1}, Brand_3 with 0.21±0.28 ng g^{-1}, Brand_4 with 2.9±3.46 ng g^{-1}, Brand_5 with 1.78±2.11 ng g^{-1}, Brand_6 with 2.97±4.43 ng g^{-1}, Brand_7 with 5.64±6.86 ng g^{-1}, Brand_8 with 3.77±4.9 ng g^{-1}, Brand_9 with 4.1±6.82 ng g^{-1}. The highest concentration of total cadmium was measured in Atlantic mackerel with 4.46±1.61 ng g^{-1} (average±SD), significantly higher than in Argentine hake with 2.49±0.89 ng g^{-1} and panga fish with 0.27±0.16 ng g^{-1}. This element is included in (EC) No 1881/2006 with the maximum value of 100 ng g^{-1} (0.1 mg kg^{-1}) allowed for fishery products and fish muscle. This element was in the ultra-trace domain proving that the products were not contaminated. In case of panga fish the exposure was significantly lower than in the two wild species captured.

Lead had no significant differences ($p>0.05$) between brands and measured samples. The values for lead reported as average±95% confidence were: Brand_1 with 3.65±6.03 ng g^{-1}, Brand_2 with 5.7±6.7 ng g^{-1}, Brand_3 with 3.9±5.4 ng g^{-1}, Brand_4 with 5.9±10.3 ng g^{-1}, Brand_5 with 3.1±5.8 ng g^{-1}, Brand_6 with 4.1±5.7 ng g^{-1}, Brand_7 with 3.59±7.2 ng g^{-1}, Brand_8 with 6.35±9.04 ng g^{-1}, Brand_9 with 5.85±7.48 ng g^{-1}.

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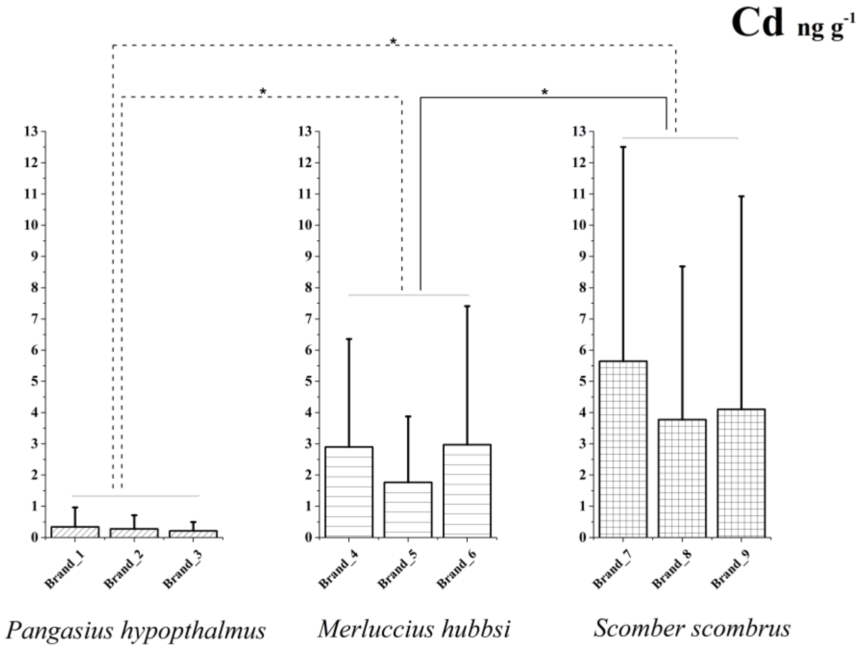

Figure 3: Concentrations of Cd from each studied brand and species, reported as average±95% confidence with the measurement unit expressed as µg g^{-1} wet weight. The comparisons between species with significant variance for Tukey test are marked with *-*p*<0.05.

The highest concentration of total lead was measured in Atlantic mackerel with 5.33±2.53 ng g^{-1} (average±SD) that was not significantly higher (p>0.05) than in Argentine hake with 4.32±2.72 ng g^{-1} and panga fish with 4.52±1.55 ng g^{-1}. This element is included in (EC) No 1881/2006 with the maximum value of 300 ng g^{-1} (0.3 mg kg^{-1}) allowed for fishery products and fish muscle. This element was in the ultra-trace domain proving that the products were not contaminated (Fig 4).

The total organic carbon (TOC) content was reported as average±SD for dry muscle. Between the brands of panga fish there were significant differences: Brand_1 with 393.7±38.2 g kg^{-1}, Brand_2 with 518 ±23.5 g kg^{-1} and Brand_3 with 328 ±37.1 g kg^{-1}. The high values in Brand_2 raise doubts about the quality. High values of TOC may be caused by a high content of fatty acids and other organic carbon compounds. The Argentine hake had significant differences between the brands: Brand_4 with 197.8±18.6 g kg^{-1}, Brand_5 with 475.3 ±11.2 g kg^{-1} and Brand_6 with 403.6 ±40.8 g kg^{-1}. The explanation for the low content in the Brand_4 may consist of the poor food resources and the fishing period when the fish was losing in weight. There were not observed significant differences for TOC in Atlantic mackerel: Brand_7 with 438.1±16.1 g kg^{-1}, Brand_8 with 405.9 ±21.8 g kg^{-1} and Brand_9 with 468.8 ±11.2 g kg^{-1}. It is known that this fish is one of the richest in fatty acids and omega 3.

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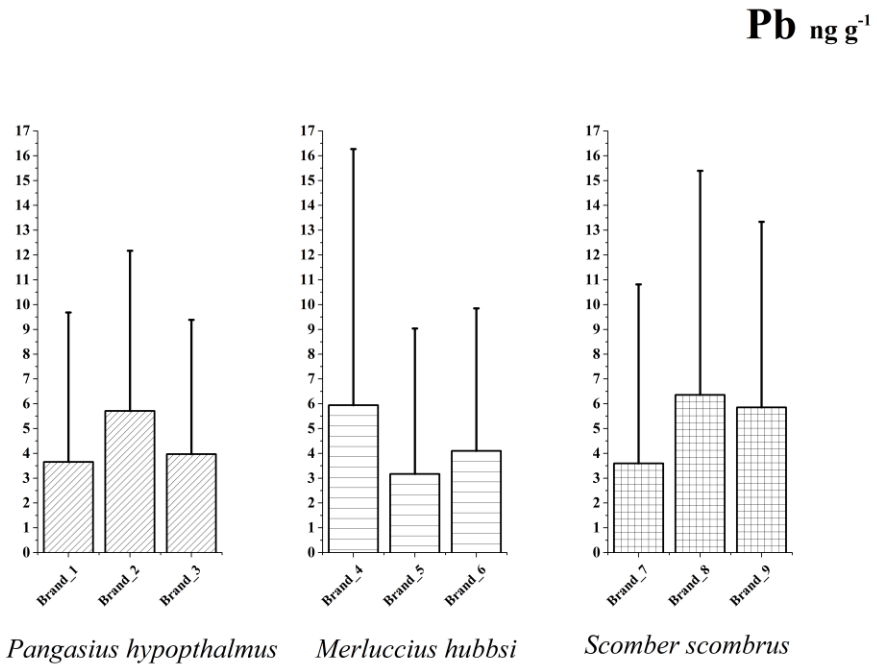

Figure 4: Concentrations of Cd from each studied brand and species, reported as average±95% confidence with the measurement unit expressed as μg g^{-1} wet weight.

The similar values obtained at this species proved that the quality was the same for all purchased brands.

Conclusions

The toxic metals did not exceed the maximum permitted values, according to EU legislation, in fish meat of the studied brands excepting the panga fish meat where the mercury concentrations in some samples reached the maximum legal limit. This raised doubts regarding the quality of the meat provided by certain brands. Cadmium and lead were in the domain of ultra-trace elements with harmless low concentrations. The Atlantic mackerel was the only species from this study with no differences between the brands regarding the toxic metal content and TOC. The consumer should have more information about the levels of possible contaminants from food to choose himself the level of exposure. From the price point of view the consumer can pay more for a quality product with less contaminants because it may require more investments. It will be not right to pay more for a low quality only to bring more profit to the sellers. This should be controlled by government authorities in any country.

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Conflict of interest

Authors declare that they have no competing interests.

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