MERCURY IN DIFFERENT MARINE FISH SPECIES ON SERBIAN MARKET

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ŽIVA U RAZLIČITIM VRSTAMA MORSKIH RIBA NA SRPSKOM TRŽIŠTU

Apstrakt

Proučavanje žive (Hg) u marinskim sistemima je od velikog interesa, s obzirom da je reč o toksičnom metalu koji ima sposobnost bioakumulacije i biomagnifikacije u lancu ishrane. Vodeni sistemi, a time i ribe, mogu biti kontaminirani živom kao posledicom zagađenja životne sredine prirodnim procesima (vulkanske erupcije, klimatske promene itd.) i antropogenim izvorima zagađenja (industrija, rudarstvo itd.). Živa (Hg) može postojati kao elementarna, neorganska i organska živa. Najtoksičniji oblik žive je metil živa (MetHg) koja čini od 70-100% ukupne Hg u ribi. Naučna ispitivanja ukazuju da velike količine žive u hrani mogu negativno uticati na razvoj fetusa i izazvati oštećenja mozga i jetre.

Cilj ovog rada bio je ispitivanje sadržaja žive u jestivim delovima tri vrste morske ribe na tržištu Srbije: oslić - *Merluccius merluccius* (n=84), skuša - *Scomber scombrus* (n=35) i papalina - *Sprattus sprattus* (n=17)). Prosečna potrošnja ribe u Srbiji iznosi oko 5 kg po glavi stanovnika, što je znatno niže u poređenju sa EU prosekom (21 kg po glavi stanovnika). Svi uzorci uzeti su i analizirani tokom 2014. godine. Analiza sadržaja žive urađena je primenom induktivno-kuplovane plazme sa masenom spektrometrijom (ICP-MS), merenjem izotopa ^{202}Hg.

Najviša srednja vrednost sadržaja žive utvrđena je u uzorcima skuše (0,056 mg/kg), zatim kod oslića (0,034 mg/kg), a najniža kod papaline (0,016 mg/kg). Maksimalno dozvoljene količine Hg u ispitanim ribama, koje su definisane zakonskom regulativom Srbije [MDK (oslić, papalina) = 500 ng/g, MDK (skuša) = 1000 ng/g] nisu prekoračene u svim ispitanim uzorcima. Statističkom evaluacijom dobijenih rezultata ustanovljeno je da postoji statistički značajna razlika ($p<0,005$) u sadržaju Hg između oslića i skuše, kao i između skuše i papaline.

Za procenu unosa Hg konzumiranjem ribe korišćeni su podaci iz „GEMS/Food Consumption Cluster Diets database". Prema ovom izvoru, procenjena prosečna nedeljna potrošnja morske ribe u Srbiji iznosi 106,4 g. Koristeći podatke iz ove studije izračunat je ne-

deljni unos Hg, baziran na srednjoj vrednosti sadržaja Hg u konzumiranoj ribi i prosečnoj telesnoj težini čoveka od 70 kg.

Na osnovu izračunatih vrednosti za nedeljni unos Hg (oslić: 0,051-0,208 µg/kg telesne težine; skuša: 0,086-0,289 µg/kg telesne težine; papalina: 0,025-0,050 µg/kg telesne težine) može se zaključiti da je unos žive pri konzumaciji oslića, skuše i papaline znatno niži od preporučenih graničnih vrednosti svetske zdravstvene organizacije (1,6 µg MetHg /kg telesne težine).

Ključne reči: živa, morska riba, tržište Srbije
Key words: mercury, marine fish, Serbian market

INTRODUCTION

The investigation of mercury (Hg) behavior in marine systems is of great interest, considering the fact that it is a toxic metal that bioaccumulates and biomagnifies over the entire marine food web (Clayden et al., 2015; Li et al., 2015). Mercury exists as metallic (elemental), inorganic and organic mercury compounds. By both abiotic and biotic processes, inorganic mercury can be transformed into one of the most toxic forms, organic Hg as methylmercury (MetHg), which is predominantly present in fish (Merritt and Amirbahman, 2009; Saei-Dehkordi et al., 2010). Depending on species, MetHg accounts for 70-100% of total Hg in fish (EFSA, 2005). Metal accumulation in fish is of global public health concern, because the consumption of contaminated fish has been associated with several diseases such as neurologically related problems, myocardial infarction and autism (Li et al., 2008). Consumption of freshwater and marine fish as well as seafood is the main environmental source of human mercury exposure (Bille et al., 2015; Vieira et al., 2015). The global increase in fish consumption tallies with trends in food consumption in general. Per capita food consumption has been rising in the last few decades. Annual fish and seafood consumption by county varies from one country to another depending on different factors such as fisheries resources, the economic climate, environmental conditions, dietary habits etc. Average annual fish consumption in Serbia is about 5 kg per capita, which is significantly lower compared to EU average of 21 kg (Baltić et al., 2009).

This study was conducted to determine and compare the content of mercury in the edible portion of three species of marine fish collected from Serbian market and ordinary consumed by the population of Serbia. On the other hand, data from this study were used in order to assess intake of Hg by fish.

MATERIALS AND METHODS

Total concentration of Hg was measured in three fish species collected in Serbian markets during 2014 year. Total 136 samples were analyzed: hake - *Merluccius merluccius* (n=84), mackerel - *Scomber scombrus* (n=35), and sprat - *Sprattus sprattus* (n=17). After collection, samples were labeled and stored in polyethylene bags and frozen at -18 °C prior to analysis. Samples were partially thawed at +4 °C 1 day before analysis. Edible parts were chopped into 2 to 3 cm thick portions and homogenized. Approximately 0.3 g of samples were mineralized by adding 5 ml nitric acid (SIGMA) and 1.5 ml hydrogen peroxide (30%,

MERCK). Microwave assisted digestion was performed in Microwave Digestion System (Via Fatebenefratelli, 1/5-24010 Sorisole (BG), Italy). The digested sample solutions were quantitatively transferred into disposable flasks and diluted to 100 ml with deionized water (ELGA).

The analysis was performed by inductively-coupled plasma mass spectrometry (ICP-MS). Measurements were performed using the instrument "iCap Q" (Thermo Scientific, Bremen, Germany), equipped with collision cell and operating in kinetic energy discrimination (KED) mode. The ^{202}Hg isotope was measured. Torch position, ion optics and detector settings were adjusted daily using tuning solution (Thermo Scientific Tune B) in order to optimize measurements and minimize possible interferences. For the qualitative analysis of the samples, five-point calibration curve (including zero) was constructed for the ^{202}Hg isotope in the concentration range of 0.2 – 2.0 mg/L. Additional line of the peristaltic pump was used for on-line introduction of multi-element internal standard (^{45}Sc – 10 ng/mL; ^{71}Ga – 2 ng/mL). Concentrations of each measured sample were corrected for response factors of both higher and lower mass internal standard using interpolation method. The quality of the analytical process was controlled by the analysis of the standard reference material (NIST SRM 1577c, Gaithersburg, USA). Measured concentrations were within the range of the certified values for all isotopes. The limit of quantification was 0,001 mg/kg.

For data analysis a one-way analysis of variance (ANOVA) and Tukey's test were used for the comparison of the mean content of Hg in different fish species, and they were performed using Minitab 16 software.

RESULTS AND DISCUSSION

Contents of Hg (mg/kg) in three edible parts of fish species as the mean value ± standard deviation (SD) are expressed, and they are graphically presented in Figure 1. Results for ANOVA and Tukey's test are showed in Figure 1, as well. Statistical analysis of the data showed significant differences ($p<0.05$) between the mercury content in hake and mackerel, as well as in mackerel and sprat. Hg limits defined by Serbian legislation (Službeni glasnik RS, 29/2014) for hake and sprat (500 ng/g fresh weight) as well as for mackerel (1000 ng/g fresh weight) were not exceeded in any of the analyzed samples.

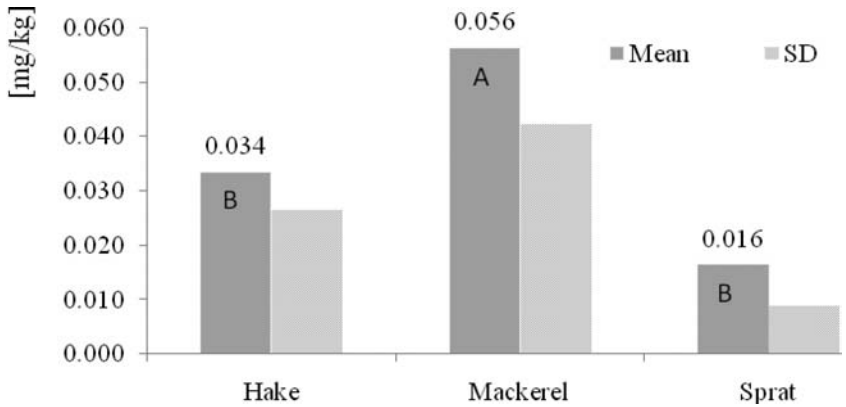

Figure 1. The mean values for Hg content (mg/kg) in three fish species [A, B – values expressed as columns followed by different letters are differ significantly ($p<0.05$)]

According to the GEMS/Food Consumption Cluster Diets database (*FAO/WHO*, 2006) the average weekly consumption of marine fish in Serbia is 106.4 g/week. Using the data of this study, the weekly intakes of Hg via three fish species consumption were calculated (Table 1). Mercury intake expressed as weekly intake (WI) was calculated using the following formula (Janković et al., 2012):

WI = (weekly consumption data x content of compound) / body weight.

Table 1. Weekly intakes (WI) of Hg via fish consumption [µg/kg b.w.]

Fish	Weekly intakes of Hg [µg/kg b.w.]			
	Mean	Maximum	Mean	Maximum
	*50% - 70 kg**		*5% - 51 kg***	
Hake	0.051	0.208	0.070	0.286
Mackerel	0.086	0.289	0.118	0.396
Spart	0.025	0.050	0.034	0.069

*body mass of 70 kg represents 50% of population (Janković et al., 2012).
*body mass of 51 kg represents 5% of population (Janković et al., 2012).

Based on epidemiological studies The Joint FAO/WHO Expert Committee on Food Additives (JECFA) established a provisional tolerable weekly intake (PTWI) of 1.6 µg MetHg/kg b.w. (FAO/WHO, 2003). The estimated weekly intakes of Hg through fish consumption among Serbian population (Table 1) are few times lower than established value.

CONCLUSIONS

Taking into consideration the results of this study, it could be concluded that the current level of total Hg in marine fish available at the Serbian market does not pose a threat to consumers' health.

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