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Element contents in commercial fish species from the Croatian market

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ABSTRACT

Concentrations of toxic (Al, As, Cd, Cr, Hg, Mn, Ni, Pb) and essential elements (Cu, Fe, Zn) were measured in 11 fish species purchased from supermarkets located in different Croatian cities. Mean element concentrations in fishes ranged: mg kg^{-1}: Al 0.13–3.5, As 0.52–3.4, Cu 0.24–0.88, Fe 2.0–19, Mn 0.095–1.6, Zn 3.4–18; μg kg^{-1}: Cd 0.61–123, Cr 5.0–41, Hg 17–130, Pb 2.0–59, Ni 5.5–51. The highest mean concentrations of elements were found in fishes: Al in cod; Cd in bluefin tuna; Cr in rainbow trout; Hg in European sea bass; Pb in canned sardine; As, Cu, Fe, Mn, Ni and Zn in sardine. Significant differences in the concentrations of all elements measured were found between fish species. Mean Cd levels of 123 μg kg^{-1} for bluefin tuna exceeded the European Commision limit of 100 μg kg^{-1}. An estimation of the dietary intake of elements associated with the consumption of the studied fish species, and its comparison with the toxicological reference values is provided. The obtained results suggest a strong reason for public concern with regard to exposure to As and Hg for consumers who often consume certain types of fishes.

1. Introduction

Fish and fishery products today are promoted and highly recommended as a food type with many positive benefits for human health, as their consumption may reduce the risk of hypertension, coronary heart disease and cancer (Mendil et al., 2010; Khawaja et al., 2014). Numerous benefits ensue from the important bioactive components of fish, such as fatty acid composition (long-chain n-3 polyunsaturated fatty acids), proteins containing all the essential amino acids, liposoluble vitamins (vitamin A, D, B12), essential elements, phytosterols, antioxidants and phospholipids (Barrento et al., 2008; Larsen et al., 2011).

Seafood and fish in marine ecosystems may be exposed to different pollutants, including toxic elements (Ikem and Egiebor, 2005). The environmental contamination by toxic elements in past decades has given rise to the significant and constant presence of an ecological and global public health concern. In this sense, numerous studies on metal content measurements have been published for a range of food types, such as fish and fish products, which can be exposed to their accumulation and may have unwanted effects on human health (Ikem and Egiebor, 2005; Tuzen and Soylak, 2007; Mendil et al., 2010; Mol, 2011; Storelli et al., 2010; Di Lena et al., 2017). Different levels of toxic metals reported have confirmed that bioaccumulation in fish tissues are due to geographic location, biotic and abiotic factors, chemistry of metals, temperature and pH value of water, characteristic of fish such as body mass, physiologic conditions, age and gender (Falco et al., 2006; Burger and Gochfeld, 2005; Castro-Gonzalez and Mendez-Armenta, 2008). Measurement of toxic element concentrations in fish in specific marine ecosystems is applicable for monitoring environmental contamination and as an indicator of pollution in the marine ecosystem (Ikem and Egiebor, 2005). Accumulation of harmful non-essential elements, such as As, Hg, Cd, Pb, Cr, Al and Ni, in aquatic organisms and consequently in fishery products may result in their transfer into the food chain, causing adverse effects on human health (Turkmen et al., 2008). Different studies have demonstrated that Hg is bioamplified along the aquatic food chain, and that predators such as high-trophic level species of shark, swordfish or tuna have concentrated levels of Hg (Storelli et al., 2010, Seixas et al., 2014). Although, Hg concentrations in different fish species is highly variable due to biotic and abiotic factors, fish consumption today is the one of the most significant sources of methylmercury accumulation exposure in humans (Burger et al., 2012). Depending on the fish species, methylmercury is accumulated between

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80% and 98% in fish (Afonso et al., 2013). Methylmercury is almost completely absorbed (95–100%) in the human digestive tract and the main target for its toxic effects is the central nervous system (Patrick, 2002). Cadmium is included in the environmental pollutants and is ranked eighth among the 20 most hazardous substances (ATSDR, 2012a). It has a long biological lifetime (20 years), and the target organs are the kidney and liver. Acute poisoning with Cd causes pulmonary oedema, bleeding, testicular damage and mortality. Long-term exposure to Cd leads to nephrotoxicity, osteotoxicity and immunotoxicity (ATSDR, 2012a). Although As can be essential, its role in the body has not yet been clarified. Its toxic effect in humans includes an effect on hormones that mediate gene transcription, mitochondrial enzymes and therefore cellular respiration, reproductive toxicity, and miscarriage, and also causes hyperpigmentation and keratosis, cardiovascular disease, neuropathy, and can affect verbal communication and long-term memory (Kapaj et al., 2006). Lead changes the function and structure of kidney, bone, central nervous system, and hematopoietic system, and produces harmful biochemical, histopathological, neuropsychological, fetotoxic, teratogenic and reproductive effects (Eisler, 2009). Chromium is considered an essential element and has an effect on carbohydrate metabolism and fat metabolism by reducing the risk of atherosclerosis development (Anderson, 1997). The toxicity of Cr is mainly due to the Cr (VI) compounds, since Cr (III) is poorly absorbed in the organism. Chromium (VI) compounds can be absorbed by the gastrointestinal tract and lungs, and even by intact skin. However, epidemiological studies carried out in the chromate production industry showed excess risks for lung cancer in workers (Tchounwou et al., 2012). Aluminium and aluminium compounds are widely used as food additives in the food industry in processing, packaging and storage, which significantly contributes to its accumulation in food in general (WHO, 2007a). May affect the reproductive system and developing nervous system. Some epidemiological studies have suggested an association between Al in drinking water and cognitive impairment, dementia and Alzheimer's disease (Krewski et al., 2007). Nickel has several possible roles in the maintenance and production of cells, and as an activator of certain enzyme systems, participates in reaction catalysed by oxidoreductases and hydrolyses (e.g. urease), is present in RNA and DNA and likely plays a role in stabilizing RNA structure, and in normal bone functioning and health. It is also an important factor in the cell membrane and lipids (Bakircioglu et al., 2011; Samal and Mishra, 2011). However, adverse health effects at higher Ni levels are related to allergic reactions, lung fibrosis, cardiovascular and kidney diseases, and lung and nasal cancers (Klein and Costa, 2007). Studies from different countries showed increased risks for lung cancer in nickel smelters and refineries (IARC, 2012).

Copper and Zn are essential elements with multiple important biochemical functions in the body, and are present in more than 300 metalloenzymes and co-factors. Copper is incorporated into a number of metalloenzymes and co-factors for several oxidative stress-related enzymes and is also used by cuproenzymes involved in redox reactions (Harvey and McArdle, 2008; Stern, 2010). Recent studies have shown that Cu also is potentially toxic because of the generation of superoxide and hydroxyl radicals, and excessive exposure may be linked to cellular damage leading to Wilson's disease or may contribute to the development of Alzheimer's disease (ATSDR, 2002; Tchounwou et al., 2008; Osredkar and Sustar, 2011). Zinc have a catalytic and structural role or regulatory roles in various cellular processes such as signal conversion and gene expression (Scherz and Kirchhoff, 2006). Excess Zn or its deficiency can lead to oxidative stress and activate or inhibit the oxidation of sensitive transcriptional factors that may affect cell function, multiplication and survival of the cells leading to disease (Oteiza et al., 2000). Iron participates in various metabolic processes in the body, including oxygen transfer, DNA synthesis and electron transfer. Iron metabolism disorders are amongst the most common human disorders and encompass a wide range of diseases with various clinical manifestations, from anaemia to neurodegenerative diseases (Evans and Halliwell, 2001; Kuvibidila et al., 2001). Excess levels of Fe in the body may have various toxic effects, or can affect the liver, heart, pancreas or lungs, and lead to various health disorders, such as diabetes mellitus, pancreatic hypertrophy and hormonal irregularities (Kang, 2001). Manganese is also an essential element, an activator of enzymes involved in catalytic and regulatory functions, and as a component of metalloenzymes (Wedler, 1994). Acute exposure to Mn may cause nervous system dysfunction. Chronic exposure at very high levels results in permanent neurological damage, which has been reported in former manganese miners and smelter workers (ATSDR, 2012b).

Present day aquaculture production volume in the European Union is about 614,191 t, with Croatia participating only with 12,043 t, in contrast to large producing countries such as the United Kingdom with 148,438 t (MA, 2015; EFSA, 2016). In 2015, production of the most common marine fish species was: 4075 t European sea bass (*Dicentrarchus labrax*), 4488 t gilthead sea bream *(Sparus aurata)*, 2603 t bluefin tuna (*Thunnus thynnus*), 67 t stone bass (*Argyrosomus regius*), 7 t turbot (*Scophthalmus maximus*), and 4 t common dentex (*Dentex dentex*) (MA, 2015).

Surveys of dietary habits conducted among the Croatian population showed that consumer fish purchase preferences were as follows: white fish 34%, blue fish 36%, cephalopods 15%, crustaceans 5%, freshwater fish 9% (Franičević, 2012). The most commonly purchased fish are sardines (*Sardina pilchardus*; 31.1%), followed by hake (*Merluccius merluccius*; 27.6%) and Atlantic mackerel (*Scomber scombrus;* 6%). The per capita consumption of fish in Croatia is about 10 kg per capita/year, less than in other European countries, such as Italy (20 kg per capita/year) or Portugal (62 kg per capita/year) (Mieiro et al., 2011; Di Lena et al., 2017).

The objectives of present study were to: i) determine the concentrations of toxic (Al, As, Cd, Cr, Hg, Mn, Ni, Pb) and essential elements (Cu, Fe, Zn) in the edible portion of different fish species purchased from supermarkets in different Croatian cities; ii) verify whether the measured concentrations of toxic elements in fish exceed the maximum prescribed levels set by the EU legislation; iii) compare the obtained element concentrations with literature data; iv) estimate the daily and weekly intake for the measured elements and compare these with the defined toxicological limits recommended by WHO and EFSA to determine a possible consumer health risk.

2. Materials and methods

2.1. Sample collection

A total of 96 samples of different fishes were purchased at the large supermarkets in capital of Zagreb, and in the cities of Split, Rijeka and Osijek in Croatia during 2016. The purchased fish consisted of species: hake *(Merluccius merluccius, n = 7),* Atlantic mackerel (*Scomber scombrus, n* = 7), cod (*Gadus morhua, n* = 7), chub mackerel *(Scomber japonicas, n = 7),* fresh and canned sardine (*Sardina pilchardus, n* = 7), European sea bass (*Dicentrarchus labrax, n* = 13), gilthead sea bream *(Sparus aurata, n* = 11*),* bluefin tuna (*Thunnus thynnus, n* = 8), salmon-bass (*Argyrosomus regius, n* = 8), rainbow trout (*Oncorhynchus mykiss, n* = 7) and carp (*Cyprinus carpio, n* = 7). Fish specimens were transported to the laboratory. Then the fish were cleaned and a portion of muscle tissue was sampled from carcass of fishes. Fish samples were than rinsed with ultrapure water and that proceeded to the draining of the liquid medium for 24 h. After that samples were homogenized. Samples of purchased canned sardines were open, also rinsed and drained until next day and then also homogenized. All homogenized fish samples were packed in prewashed polyethylene bags and coded for identification.The samples were kept stored and frozen at −18 °C until analysis.