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Original Article

Assessment of essential elements in the wild Beluga Sturgeon (*Huso huso*) caviar from Caspian Sea

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Abstract: In this study, the concentration of Calcium (Ca), Cobalt (Co), Chromium (Cr), Copper (Cu), Iron (Fe), Potassium (K), Magnesium (Mg), Manganese (Mn), Selenium (Se) and Zinc (Zn) as essential metals, were determined in caviar of wild beluga sturgeon caught from the Caspian Sea in March 2012. Potassium (4885.51± 17.81 $\mu g\ g^{-1}$) and Magnesium (346.61± 6.6 $\mu g\ g^{-1}$) had the highest concentration and Cobalt and Manganese levels were less than 0.01 $mg\ kg^{-1}$ wet weight. The mean concentration of Copper and Zinc in the caviar samples were under the permissible limits proposed by the UK's Ministry of Agriculture, Fisheries and Foods. The caviar maximum allowable daily consumption rate was calculated. However, the health risks from caviar consumption are uncertain because the amount of caviar consumed by heavy users is not known.

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Introduction

Trace metals (e.g., arsenic, copper, iron, molybdenum, tin, etc.) are essential components of the hydrosphere and are necessary for normal metabolism of organisms in low concentration; however, elevated concentrations in tissues might be toxic for biological activities (Joyeux et al., 2004). The rapid development of industry and agriculture has increased the heavy-metal pollution, which can be intensely accumulated and biomagnified in the water, sediment, and aquatic food chains (Yi et al., 2011).

Sturgeons are the principal source of the most valuable food, i.e. caviar (Speer et al., 2000) and the Caspian Sea have supplied more than 95% of world's caviar output (Mashroofeh et al., 2012). On the other hand, this lake receives the huge amount of pollutants including petroleum products, organic substances, metals and nitrogen compounds (UNEP, 2008). Six sturgeon species also exist in the Caspian Sea that four of them, including Persian sturgeon, *Acipenser persicus*; Russian sturgeon, *A. guildensteidti*; stellate sturgeon, *A. stellatus*; and beluga sturgeon, *Huso huso* are commercially valuable (Agusa et al., 2004; Pourang et al., 2005). Overfishing of sturgeon for caviar and meat, loss of habitat due to the construction of dams on the Caspian Sea tributaries, and elevated levels of pollutions have been led to great decline in their population (IUCN, 2012a).

Caviar of beluga is the most coveted of all caviar (Speer et al., 2000). On the other hand, beluga as a predator, is at the top trophic level feeding on many fish species such as Caspian roach (*Rutilus caspicus* L.), common carp (*Cyprinus carpio* L.) and kilka (Clupeonella), and have the longest life time (Mashroofe et al., 2012; IUCN, 2012b). Because of bioaccumulation through the food web, it is expected high levels of contaminants, such as metals, in beluga sturgeons (Wang et al., 2008). Some methods

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have been proposed for potential risks estimation to human health due to heavy metals in food. These risks may be divided into two groups, including carcinogenic and non-carcinogenic impacts (Yi et al., 2011). Risk assessment is one of the fastest methods, which is required to investigate the effect of the hazards on human health and to determine the level of treatment, which tends to solve the environmental issues that occur in daily life (Amirah et al., 2013).

Therefore, the objectives of the present study were to determine the concentration of Ca, Co, Cr, Cu, Fe, K, Mg, Mn, Se and Zn in the caviar samples of wild beluga sturgeon and also compare the results obtained in other studies regarding metal levels; moreover, the potential human health risk due to the caviar consumption is evaluated.

Material and methods

Sample collection: A total of nine wild beluga sturgeons (with mean weight of 73.2 ± 8.2 kg) were caught by the Shahid Marjani hatchery center (Gorgan, north of Iran) from the southeastern coast of the Caspian Sea in March 2012. The specimens were washed and gutted on the site under hygienic conditions. Then, 65 g of roe ("caviar") free of the egg sack membrane were removed from each female, placed into separate 100 ml plastic containers with lids and immediately transported to the laboratory in an insulated box with a suitable quantity of flaked ice to completely cover the containers and kept frozen at -40°C in a freezer until analyzed.

Determination of trace elements: The samples were analyzed three times for Ca, Co, Cr, Cu, Fe, K, Mg, Mn, Se and Zn by inductively coupled plasma-optical emission spectrophotometer (ICP-OES) (Optima 2100DV, Perkin Elmer Inc., Waltham, MA, USA) as described by Türkmen et al. (2009). Briefly, about 5 g of homogenized caviar (using a blender Panasonic, MJ-W176P, Osaka, Japan) was mixed with 50 ml of ultrapure concentrated HNO_3. The mixture was heated on a lab digital heater (IKA, Staufen, Germany) to 100-150ºC for about 2 hrs until the tissue dissolved and the solution evaporated to near dryness. All organic materials in each sample were completely digested by repeating the digestion twice more. After cooling, 5 ml of 1 N HNO_3 was added to the digested residue. Afterward, it was transferred to a 25 ml volumetric flask and brought to level with by purified water with conductivity under 0.05 µS (Millipore system, Eschborn, Germany). The recoveries of the metals were assessed by adding increasing amounts of each element to samples (spiking method), which were then taken through the digestion procedure. The resulting solutions were analyzed for their metal concentrations. Recoveries of the metals ranged from 96.8-102%. In this study, metal concentrations were determined as mg kg^{-1} wet weight of roe.

Risk assessment: Since, there is not information about caviar consumption, the maximum allowable daily consumption rate (MADCR) for each metal was used for chronic non-cancer health risk assessment. The MADCR (g/day) for caviar consumption was calculated using the following equation (Wang et al., 2008): $MADCR = 10^6 \times HQ \times RfD \times (BW/C)$, where HQ (hazard quotient) = 1; RfD is the reference dose (mg/kg/day) set by US EPA(2011); BW is the body weight of 70 and 14.5 kg for an adult and child, respectively, and C is the metal concentration in the caviar samples (mg kg^{-1}) and the constant adjusts for concentration conversions. Also, the metal levels in caviar samples were compared with the guidelines proposed by MAFF (2000).

Results and discussion

Metal concentration: Mean levels of essential metals in caviar of wild beluga are shown in Table 1. Among the measured metals, K (4885.51 ± 17.81 µg g^{-1}) and Mg (346.61± 6.6 µg g^{-1}) had the highest levels, and Se (0.9 ± 0.042 µg g^{-1}) had the lowest level. Also, the averages of Co and Mn were below detection limits in the samples. In another experiment conducted by Wang et al. (2008), K (1.4 ± 0.2 µg g^{-1}), Mg (0.25 ± 0.02 µg g^{-1}), Ca (0.10 ± 0.03 µg g^{-1}), and Fe (0.06 ± 0.05 µg g^{-1}) had the

Table 1. Average (±SD) metal levels (µg g-1 wet weight) in caviar of wild beluga sturgeon (*Huso huso*; n=9).

Ca	Co	Cr	Cu	Fe
51.7(±0.62)	<0.01	0.28(±0.026)	1.27(±0.15)	65.61(±0.45)

K	Mg	Mn	Se*	Zn
4885.51(±17.81)	346.61(±6.6)	<0.01	0.90(±0.042)	24.32(±0.23)

*ng g^{-1} wet weight

Table 2. Maximum allowable daily consumption rate (MADCR) estimates for children and adults using median concentration (mg kg^{-1} wet weight)[1].

Metals	RfD[2] (mg/ kg/ day)	MADCR (g/day)	
		Children	Adult
Cr(III)	1.50E+00	77700	375000
Cu	4.0E-02	460	2210
Fe	7.0E-01	155	747
Mg	4.90E+01	205	990
Se*	5.00E-03	80600	389000
Zn	3.00E-01	180	863

[1]Data arranged by three significant figure
[2]Reference doses of metals set by EPA (2011)
*ng g^{-1} wet weight

highest levels in the caviar samples. Some nutrients such as calcium, iron, magnesium, and potassium are essential elements required to maintain cellular function in the roe (Hui, 2006; Wang, 2008).

Gessner et al. (2002) detected Cu and Zn levels of 1.45 and 11.60 µg g^{-1} wet weight in beluga fresh caviar samples from the Caspian Sea. Sadeghi Rad et al. (2005) also found Cu and Zn levels of 1.74-6.8 and 33.8-131.2 µg g^{-1} wet weight, respectively, in caviar samples of wild Persian sturgeon from southern Caspian Sea that were higher than the results of the present study. In the current finding, Zn level was higher than the results were reported by Wang et al. (2008) in caviar of beluga sturgeon from southern Caspian Sea; however, our finding showed that Cu and Zn concentration were lower than the dietary guidelines for fish, as represented by MAFF (2000) (Standard: Cu: 20 µg g^{-1}ww ; Zn: 50 µg g^{-1} ww). According to literature, Cu and Zn levels in fish gonads may increase during the pre-spawning period, and eggs contain large amounts of both metals (Atukorala and Waidyanatha, 1987; Zubcov et al., 2012). It seems that contents of some metals such as copper and zinc in fish and other aquatic vertebrates are modified by diet, age of the organism, reproductive state, and other variables (Elsier, 1993). In comparison to our results, levels of Cu (0.7-1.6 µg g^{-1} ww), K (1017-1603 µg g^{-1}ww), Mg (230.1-266.0 µg g^{-1}ww) and Zn (16.8-24.0 µg g^{-1}ww) were detected by Wang et al. (2008) in Eurasian caviar that were lower than our results, and concentrations of Ca (56.8-173.9 µg g^{-1}ww), Co (5.2-23.9 ng g^{-1} ww), Mn (0.8-1.4 µg g^{-1}ww) and Se (1.0-2.1µg g^{-1} ww) that were higher, and Fe levels (21.6-155.1 µg g^{-1}ww) that was comparable. These differences may be interpreted by many factors such as habitat, seasonal variations, individual affinity for metal uptake and dietary habits that influence on variations observed in metal concentrations among sturgeon species (Papagiannis et al., 2004). On the other hand, the difference of physiological features of different fish tissue can affect on the accumulation of a particular metal (Pourang et al., 2005). In other words, biomonitoring using caviar may not be effective for some contaminants, including some essential metals such as Ca, Co, Cu, K, Mg and Zn that may accumulate in other organs like liver (Wang et al., 2008), and the increased levels may reflect the elevated requirement of sturgeons for these components (Gessner et al., 2002). Concentrations of essential metals are regulated by physiological mechanisms in fish (Pourang et al., 2005); however, they are regarded as potential risks that can endanger both fish and human health (Yilmaz et al., 2007).

Health risks: Table 2 shows the toxicity information and the estimated MADCR. Analysis of risk is important due to the health benefits of consuming caviar, which is considered to be a nutritious food. The rate of caviar consumption is unknown; therefore, the health risks calculation of caviar consumption are impossible. However, the MADCR provides an approach to evaluate its potential importance (Wang et al., 2008). The MADCR shows an average daily consumption rate that would not be expected to cause adverse non-carcinogenic health effects (EPA, 2000). In this study, for adult chronic non-cancer health effects using a HQ of 1, the MADCR is relatively low for Fe and Zn especially for children. In comparison to our result, Wang et al. (2008) estimated the MADCRs for Cr (358×10^4 g/day for children; 1727×10^4 g/day for adult) that was higher, Zn (200 g/day for children; 980 g/day for adult) that was comparable, and Se (53 g/day for children; 980 g/day for adult) that was more restrictive. Because of the difference in body weight, the MADCRs for children are about five times lower than for adults; although the same per kg values are used as insufficient work has been done to generate separate values for children.

In conclusion, this study analyzed the concentration of some essential metals (Co, Cr, Cu, Fe, K, Mg, Mn, Se and Zn) in caviar samples of wild beluga sturgeon. The Caviar consumption rate is expected to be very low, and regarding to health benefits of consuming caviar, it seems that consumption of this food does not pose any danger for human health.

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