

## Selected Metals in Canned Fish Consumed in Iran

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### ABSTRACT

**Background:** The presence of heavy metals in the environment could constitute a hazard to food security and public health. These can be accumulated in aquatic animals such as fish. Canned fish is consumed regularly in many countries. In this study, the levels of heavy metals Cu, Ni, Fe and Cr were evaluated in commercial canned fish products that are commonly consumed in Iran. The canned fish studied were longtail tuna, Kawakawa, Kilka and yellowfin tuna.

**Methods:** Samples of four popular brands of canned fish in the Iranian market (yellowfin tuna, common Kilka, Kawakawa and longtail tuna) were analyzed for levels of Cu, Ni, Fe and Cr after wet digestion with acids using graphite furnace atomic absorption spectrophotometry.

**Results:** The mean concentrations for the metals in the different brands were: For Cu: 0.91, 0.73, 1.18 and 0.84  $\mu\text{g g}^{-1}$  for brands A, B, C and D respectively. For Ni: 0.37, 0.19, 0.14 and 0.18  $\mu\text{g g}^{-1}$  for brands A, B, C and D respectively; For Fe: 45.9, 34.0, 77.53 and 61.3  $\mu\text{g g}^{-1}$  for brands A, B, C and D respectively. For Cr: 2.57, 3.24, 3.16 and 1.65  $\mu\text{g g}^{-1}$  for brands A, B, C and D respectively. Significant differences were observed in the heavy metal levels between all of the different brands of canned fish evaluated in this study.

**Conclusion:** The metal concentrations for the varieties of canned fishes were generally within the FAO/WHO, U.S. FDA and U.S. EPA recommended limits for fish except for Iron for which all different Brands exceeded the limit.

**Keywords:** Chromium, Copper, Food Security, Iranian Market, Iron, Nickel.

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### INTRODUCTION

Trace metals are generally released into aquatic environments in different ways and accumulation of these metals is dependent on the concentration of the metal and the exposure period [1].

Metal pollution in the marine environment is not that apparent but its impacts on delicate marine ecosystems and humans are drastic. Heavy metals burdens in fish follow a multivariate dependence pattern. Fish can accumulate substantial amounts of metals in their tissues especially muscles and this, can represent a major dietary source of these metals for humans [2, 3]. High levels of heavy metals in fish, sea foods and fish products have been widely reported [1, 4-22].

Trace metals are significant either from the viewpoint of their essentiality or their toxicity [23, 24]. Low or high trace elements imbalances can be considered as risk factors for several diseases. Metals, such as iron (Fe), copper (Cu), zinc (Zn) and manganese (Mn), are essential metals since they play important roles in biological systems [13]. Cu is known to be essential and may enter foodstuff during its processing or by environmental contamination. Cu is an essential constituent of metalloenzymes and is required for hemoglobin synthesis and catalysis of metabolic reactions [25]. However, Cu ions such as  $\text{Cu}_2\text{OH}^+$  and  $\text{CuOH}^+$  are toxic to the fish [26]. Trace amounts of nickel (Ni) act as activator of some enzyme systems but its toxicity at higher levels is of concern and it accumulates in the lungs and frequently causes bronchial failure. In addition to environmental

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contamination of Ni in foods, it can also get into foods through processing activities such as canning and cooking in Ni containing vessels. Based on the U.S. EPA with an oral reference dose of  $20 \mu\text{g kg}^{-1} \text{ day}$ , a provisional maximum tolerable daily intake of 1.2 mg Ni /person/day can be estimated [12]. Fish is a major source of iron for adults and children. Iron deficiency causes anemia [15]. Iron is a vital component for human life and the human body contains 60-70  $\mu\text{g g}^{-1}$  of iron. Most importantly, the Fe compounds, specially hemoglobin and myoglobin are essential for human survival. Chromium (Cr) is widely distributed in human tissues in extremely low and variable concentrations. Chronic exposure to high levels of Cr has been correlated with lung cancer in humans and kidney damage in animals [27].

Canned fish is consumed regularly in many countries, including Libya, USA, Portugal, the Kingdom of Saudi Arabia, Turkey and Iran [4, 7- 9, 12]. Therefore, in this study, the levels of the heavy metals Cu, Ni, Fe and Cr were evaluated in commercial canned fish products that are commonly consumed in Iran, where such data is unavailable. The canned fish studied were longtail tuna, Kawakawa, Kilka and yellowfin tuna. It is hoped that these results will provide the data necessary for the assessment of toxic metal intake from this source for Iranians.

## MATERIALS AND METHODS

### Sample Collection

During the year 2012, 120 samples of four different Iranian brands (30 samples for each brand) were obtained: "Famila Co." (Tehran), yellowfin tuna (*Thunnus albacares*) [Brand A]; "Shilaneh Co." (Qazvin), common Kilka (*Clupeonella cultriventris caspia*) [Brand B]; "Pars Tuna Co." (Bushehr), Kawakawa (*Euthynnus affinis*) [Brand C], and "Hiltune Co." (Tehran), longtail tuna (*Thunnus tonggol*) [Brand D] of canned fish (185 g cans) were analyzed for their content of Cu, Ni, Fe and Cr. These 120 canned fish samples were procured from groceries, markets, supermarkets, hypermarkets and main food distribution networks in Tehran between February and April 2012.

### Chemical Analysis

All glassware was cleaned by soaking overnight in 10% nitric acid, followed by rinsing with distilled water. The acids used for wet

digestion were of high purity Ultrex (Merck, Germany) grade, while the distilled water was further deionized (SKU: D4521). The blank values were below the detection limits of the instrument. Working standards were made from the stock by dilution of the measured aliquots with 1.0M nitric acid. Spectrophotometric analysis was performed at the most sensitive setting for each metal. Each sample was analyzed in triplicates and the results, which mostly agreed within  $\pm 1.0\%$ , were averaged. A reagent blank determination was carried out with every batch of 10 samples.

After opening each can oil/broth was drained off and the meat was homogenized thoroughly in a food blender (Hongdun HWT). Samples were then digested without delay in quartz Erlenmeyer flask with 15 ml of a Suprapure nitric:perchloric:sulphuric acid (25 + 25 + 1 v:v:v) mixture. About 5 g of sample were digested, using a hot plate at  $150^\circ\text{C}$ . Further aliquots of nitric acid were added until a completely colorless solution was obtained. After evaporation using Perkin Elmer Multiwave 3000, the residue was dissolved in 10 ml of water with 1ml of conc. Suprapure HCl at  $100^\circ\text{C}$ . Finally, the volume was made up to 25 ml with deionized water. Determination of Cu, Ni, Fe and Cr were done by direct aspiration of the sample solution into the air-acetylene flame of the atomic absorption spectroscopy (4110 ZL, Perkin Elmer) [12].

### Statistical Analysis

One-way analyses of variance (ANOVA) and Tukey test were used to determine whether Cu, Ni, Fe and Cr concentrations varied significantly between species, and values less than 0.05 ( $p < 0.05$ ) considered statistically significant. The statistical calculations were done using SPSS 15.0 version (SPSS Inc., Chicago, IL, USA) statistical package.

## RESULTS

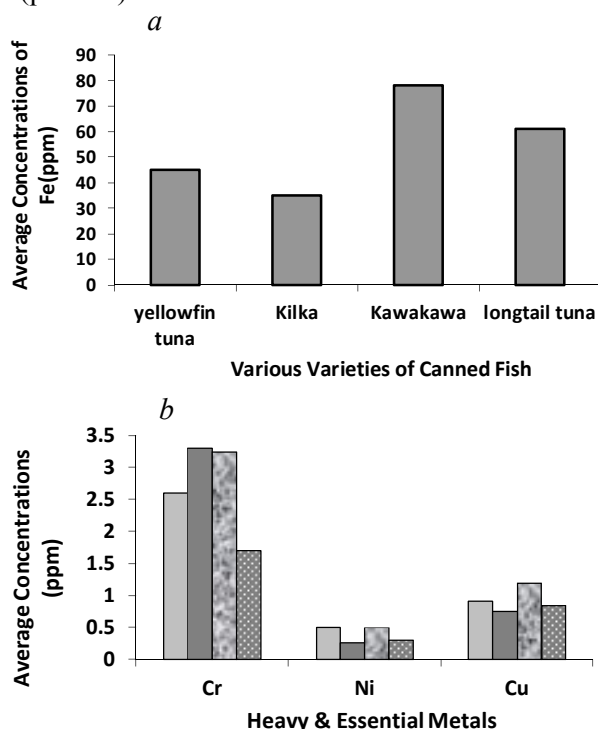
The concentrations of Cu, Ni, Fe and Cr in canned fish are presented in Table 1 along with the statistical parameters. Thirty samples for each canned fish were analyzed to assess the amounts of these metals.

**Table1.** Metal contents ( $\mu\text{g g}^{-1}$ ) in various varieties of canned fish.

Metal	yellowfin tuna		Kilka		Kawakawa		longtail tuna	
	Range	Mean $\pm$ SD	Range	Mean $\pm$ SD	Range	Mean $\pm$ SD	Range	Mean $\pm$ SD
Cu	0.53-1.83	0.91 $\pm$ 0.49 <sup>a</sup>	0.43-1.0	0.73 $\pm$ 0.39 <sup>b</sup>	0.9-1.43	1.18 $\pm$ 0.43 <sup>d</sup>	0.5-1.1	0.84 $\pm$ 0.61 <sup>c</sup>
Ni	0.02-0.75	0.37 $\pm$ 0.12 <sup>d</sup>	0.02-0.65	0.19 $\pm$ 0.12 <sup>c</sup>	0.02-0.7	0.14 $\pm$ 0.11 <sup>a</sup>	0.01-0.55	0.18 $\pm$ 0.12 <sup>b</sup>
Fe	15.85-88.22	45.87 $\pm$ 11.15 <sup>b</sup>	14.25-55.75	34.02 $\pm$ 9.82 <sup>a</sup>	26.75-222.82	77.53 $\pm$ 57.22 <sup>d</sup>	9.27-99.97	61.30 $\pm$ 51.16 <sup>c</sup>
Cr	0.85-4.67	2.57 $\pm$ 1.87 <sup>b</sup>	1.17-6.47	3.24 $\pm$ 2.35 <sup>d</sup>	1.55-4.42	3.16 $\pm$ 2.97 <sup>c</sup>	0.57-3.02	1.65 $\pm$ 1.49 <sup>a</sup>

Vertically, letters a, b and c show statistically significant differences ( $p < 0.05$ ).

Statistical analyses of the data for yellowfin tuna showed no significant differences among all samples. For Kilka, the concentration of Cu was lower in magnitude compared to the other canned fish evaluated in this study. Figure 1a, b shows the comparative levels of Cu, Ni, Fe and Cr in the various varieties of canned fish. It can be seen that the average concentrations Fe in Kawakawa is more than 2 times higher than Kilka. Similarly the Cu for Kawakawa is much higher than Kilka as well. On the other hand, the average Ni content in Kawakawa was much lower than in yellowfin tuna. Similar behavior is shown by Fe and Cu. The comparison of the average concentrations of each element in different brands of canned fish by ANOVA and the Tukey test are shown in table 1. The results indicated that there were significant differences within and between all of the evaluated brands ( $p < 0.05$ ).



**Figure 1a, b.** Comparative levels of selected heavy and essential metals in canned fish.

## DISCUSSION

The levels of heavy metals in the fish depend upon many factors like the duration of exposure of fish to contaminants in the water, the feeding habits of each fish species, the concentrations of contaminants in the water column, water chemistry, any contamination of fish during handling and processing, and fish sex, weight, and season [15]. According to Taha'n et al. (1995), the pH of the canned product, the quality of the lacquer coatings of canned products, oxygen concentration in the headspace, quality of coating and the place of storage place may control the metal levels in canned fishes for those metals found in the canning material [28]. Iron deficiency causes anemia and the fish are major dietary sources for this important nutrient [8]. However, it is also known that when the intake of Fe is more than  $15.0 \mu\text{g g}^{-1}$ , it can produce toxic effects [12, 25]. Ponka et al. (2007) emphasized that mammals are not able to excrete excess iron, and chronic iron overload is associated with a slowly progressing failure of various organs [29]. Levels of Fe in canned fish show a wide variation around the world, ranging from 2.95 to  $64.1 \mu\text{g g}^{-1}$  [12]. The Fe levels in the literature have been reported to be between  $59.6\text{--}73.4 \mu\text{g g}^{-1}$  for muscles of fish from the Mediterranean sea [3],  $68.6\text{--}163 \mu\text{g g}^{-1}$  for muscles of fish from the Black and Aegean Seas [30],  $30\text{--}160 \mu\text{g g}^{-1}$  for muscles of fish from the Black Sea coasts [31],  $4.83\text{--}29.2 \mu\text{g g}^{-1}$  in canned sardines marketed in USA and  $21.0\text{--}88.8 \mu\text{g g}^{-1}$  in canned sardines marketed in Brasilia [5, 8]. The average concentrations of this metal have been reported to be  $10.2 \mu\text{g g}^{-1}$  in canned bonito [32] and  $16.2 \mu\text{g g}^{-1}$  in canned mackerel [8]. In this study, the average Fe concentrations were  $45.9 \mu\text{g g}^{-1}$  for the samples of *Thunnus albacares*,  $34.0 \mu\text{g g}^{-1}$  for *Clupeonella cultriventris caspia*,  $77.5 \mu\text{g g}^{-1}$  for *Euthynnus affinis* and  $61.3 \mu\text{g g}^{-1}$  for *Thunnus tonggol*, all of which were above the

Turkish permissible limit ( $15.0 \mu\text{g g}^{-1}$ ). In a similar study, Ikem and Egeibor (2005) reported that the average content of Fe in canned tuna, from Georgia and Alabama in the US, was  $15.8 \mu\text{g g}^{-1}$ , but they mentioned that some samples contained up to  $88.4 \mu\text{g Fe g}^{-1}$  [8]. Therefore, it is clear that the Fe levels of many canned tuna samples are above the limits suggested by the Turkish government. In a study in the US [33], the levels of Fe in canned salmon was found to be  $6.0 \pm 0.9 \mu\text{g g}^{-1}$ , which is lower than most other published work.

It is known that seafood is a good source of dietary Cu, which is an essential element for humans but again very high intake ( $>120 \mu\text{g g}^{-1}$ ) can cause adverse health problems, such as liver and kidney damage [8, 25, 34]. Whereas the FAO (1983), WHO (1996) and Maff (1994) permit levels up to  $30 \mu\text{g g}^{-1}$  [34-36], the literature values ranged from  $0.23$  to  $9.49 \mu\text{g g}^{-1}$  for muscles of fish from the Marmara Sea [37],  $0.7$ - $27 \mu\text{g g}^{-1}$  for muscles of fish from Lake Budi [38],  $0.74$ - $2.24 \mu\text{g g}^{-1}$  for muscles of fish from Iskenderun Bay [39],  $0.15$ - $5.06 \mu\text{g g}^{-1}$  for muscles and whole fish from Turkish seas [40],  $0.32$ - $6.48 \mu\text{g g}^{-1}$  for muscles of fish from the Marmara, Aegean and Mediterranean Seas [41]. Tüzen and Soylak (2007) studied the Cu content in four samples of canned bonito and reported the average to be  $1.28 \mu\text{g g}^{-1}$  [32]. For canned sardines marketed in Brasilia and in the USA, Cu contents have been reported to be between  $1.31$  and  $2.25$  [5] and  $0.50$ - $1.75 \mu\text{g g}^{-1}$  [8], respectively. Likewise, the average amounts of Cu in canned sardines consumed in the Kingdom of Saudi Arabia have been reported as  $2.26 \mu\text{g g}^{-1}$ , while  $1.96 \mu\text{g g}^{-1}$  were found for Cu in canned sardines in Turkey [12, 32]. In canned mackerel, the concentration of Cu has been reported as  $0.81 \mu\text{g g}^{-1}$  by Ikem and Egeibor (2005). All these findings are similar to the current results and show that Cu in canned fish is well below the recommended limits (Table 1).

Levels of Ni in canned fish from Denmark and Nigeria were  $0.20 \mu\text{g g}^{-1}$  and  $3.11 \mu\text{g g}^{-1}$  respectively. Our values compared well with those from Denmark but were significantly lower than those reported from Nigeria (Table 1). In the literature Ni levels ranged from  $<0.01$  to  $2.04 \mu\text{g g}^{-1}$  for muscles of fish from the Black Sea coast [31],  $0.66$  to  $1.59 \mu\text{g g}^{-1}$  for muscles of fish from Iskenderun Bay (Turkmen et al.,

2006),  $0.02$ - $4.22 \mu\text{g g}^{-1}$  for muscles of fish from the coastal waters of the Turkish seas [41],  $0.02$ - $3.97 \mu\text{g g}^{-1}$  for muscles of fish from the Marmara, Aegean and Mediterranean seas [28].

Chromium (III) is an essential nutrient that helps the body use sugars, proteins, and fats but Cr (VI) is carcinogenic [42]. Excessive amount of Cr (III) may cause adverse health effects [41]. In the literature, Cr levels in fish have been reported to be in the range of  $0.06$ - $0.84 \mu\text{g g}^{-1}$  for muscles of fish from the Black Sea coasts [31],  $0.10$ - $1.60 \mu\text{g g}^{-1}$  for muscles of fish from the Turkish seas [40],  $0.04$ - $1.75 \mu\text{g g}^{-1}$  for muscles of fish from the Marmara, Aegean and Mediterranean Sea [41],  $0.310$ - $0.73 \mu\text{g g}^{-1}$  for muscles of fish from the western coast of the United Arab Emirates [43] and  $0.2$ - $1.87 \mu\text{g g}^{-1}$  for muscles of fish from Indian fish markets [44].

## CONCLUSION

The results from this study suggested that significant differences existed in the metal concentrations across different canned fish types in Iran. Also, analytical data obtained from this study shows that the metal concentrations for the varieties of canned fishes except for Fe (because Fe may have been contributed by the enamel of the cans in which the canned fish was processed) were generally within the FAO/WHO, U.S. FDA and U.S. EPA recommended limits for fish, i.e., for Fe ( $15.0 \mu\text{g g}^{-1}$ ), Cr ( $8.0 \mu\text{g g}^{-1}$ ) and Cu ( $120 \mu\text{g g}^{-1}$ ) [25]. There is therefore no serious health risk associated with the consumption of the four studied metals in the canned fishes analyzed. Both low-risk groups (adolescents and adults) and high-risk groups (pregnant mothers and children) must, based on the results obtained, reduce their consumption of canned fish if they are at risk for Fe excess as frequent consumption may result in bioaccumulation of Fe and increased health risks. Therefore more research and assessments of seafood quality is needed in many countries to provide more data and help safeguard the health of humans.

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