Original Article

Determination of some heavy metals in canned Sardines fish from Iraqi markets

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Abstract:

Background: Canned fish is consumed regularly in all countries. The levels of heavy metals which are present in the environment could constitute a hazard to food security and public health. These can be accumulated in aquatic animals such as fish.

Objective: In this study, selected heavy metals: Copper (Cu), Nickle (Ni), Chromium (Cr) and Iron (Fe) were evaluated in commercial canned fish products (Sardines) that are commonly consumed in Iraq. The canned fish (Sardine) which studied were Yacout Sardine (Morocco), Marina Sardine (Tunisia), Silver Sardine (Morocco) and Salsa Sardine (China).

Methods: Prospective study was done in Baghdad from January to June 2016 . 40 samples of four different foreign brands (10 samples for each brand were obtained): Yacout Sardine (Morocco), Marina Sardine(Tunisa), Silver Sardine (Morocco) and Salsa Sardine (China) of canned fish (90 g cans) were analyzed for their content of Cu, Ni, Cr and Fe. Atomic absorption spectroscopy technique was used for determination of metals under study.

Results: Mean levels of Cu in four types of canned sardine were 0.7±0.03 µg/g in Yacout canned sardine, 0.9±0.0303 µg/g in Marina canned sardine, 2.1±0.367 µg/g in silver canned sardine and 1.0±0.41 µg/g in Salsa canned sardine, while mean levels of Ni in four samples were 0.14±0.043 µg/g, 0.12±0.035 µg/g ,0.12±0.055 µg/g and 0.14±0.0285 µg/g .Also mean levels of Cr in same four samples were 0.1±0.0332 µg/g, 0.08±0.02 µg/g, 0.1±0.0245 µg/g, 0.11±0.0274 µg/g. and mean levels of Fe in four samples were 21±1.685 µg/g , 25±1.1 µg/g , 20±1.886 µg/g and 30±0.831 µg/g respectively

Conclusion: analytical data obtained from this study shows that the metal concentrations for the types of canned sardines except Fe were generally within the Environmental Protection Agency in United States of America (U.S.EPA), Food and Agriculture Organization (FAO),World Health Organization(WHO) and Food and Drug Administration in United States of America (U.S.FDA) recommended limits for canned fish and do not cause any risk for the local consumers, but contamination of Fe in majority of canned sardines samples may cause risk for the consumers.

Keywords: Copper, Nickel, Chromium, Iron, Food Security.

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Introduction:

One of the most serious problems facing the world is contamination of the environment by inorganic, organic, and organometallic materials. There has been growing interest in monitoring of heavy metals in the bioorgans(1-2). 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(3).There have been many reports on contamination of fish by chemicals in the environment(4). Heavy metals are considered the most important constituents of pollution from aquatic environment and sea because of their toxicity and accumulation by marine organisms,such as fish (5). 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. High levels of heavy metals in fish, sea foods and fish products have been widely reported(6). Low or high trace element's imbalances can be considered as risk factors for several diseases. Metals, such as zinc (Zn) , copper (Cu), iron (Fe), are essential metals since they play important roles in biological systems(7). Iron is a vital component for human life and the human body contains 60-70 µg /gm of iron. Most importantly, the Fe compounds, specially hemoglobin and myoglobin are essential for human survival. Fish is a major source of iron for adults and children. Iron deficiency causes anemia(8).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. However, Cu ions such as Cu2OH+ and CuOH+ are toxic to the fish . Chromium (Cr) is widely distributed in human tissues in extremely low and variable concentrations. Chronic

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exposure to high levels of Cr has been correlated with lung cancer in humans and kidney damage in animals (6). 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 contamination of Ni in foods, it can also get into food through processing activities such as canning and cooking in Ni containing vessels. Based on the Enviromental Protection Agency in United States of America (U.S. EPA) with an oral reference dose of 20 µg/kg day, a provisional maximum tolerable daily intake of 1.2 mg Ni /person/day can be estimated(9). Some elements like Manganese (Mn) and Zinc (Zn) are essential functional and structural elements in biological systems(10). Canned fish is consumed regularly in many countries, including Libya, USA, Portugal, the Kingdom of Saudi Arabia, Turkey and Iran(9). The aim of this study, levels of the heavy metals Cu, Ni, Cr and Fe were evaluated in commercial canned fish products that are commonly consumed in Iraq, where such data is unavailable. The canned fish studied were Yacout Sardine (Morocco), Marina Sardine(Tunisa), Silver Sardine (Morocco) and Salsa Sardine (China). It is hoped that these results will provide the data necessary for the assessment of toxic metal intake from this source for Iraqi people.

Materials and methods:-

Sample collection:- Fourty samples of four different foreign brands (10 samples for each brand were obtained): Yacout Sardine (Morocco), Marina Sardine(Tunisa), Silver Sardine (Morocco) and Salsa Sardine (China) of canned fish (90 g cans) were analyzed for their content of Cu, Ni, Cr and Fe. These 40 canned fish samples were procured from markets, supermarkets and main food distribution networks in Baghdad from January to June 2016._

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 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 ±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 ◦C.

Further aliquots of nitric acid were added until a completely colorless solution was obtained. After evaporation using Perkin Elmer Multiwave3000, the residue was dissolved in 10 ml of water with 1ml of conc. Suprapure HCl at 100◦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) (9).

Statistical analysis:-

Statistical analysis of data was obtained by using the Statictical Package for Social Science (SPSS) version (10) and Microsoft Excel (2007) software .descriptive statistics for all data of each set were expressed as mean ± SD, student's t- test was used to evaluate the significance of differences between concentration levels of each metal in four types of canned sardines.

Results:-

The concentrations of Cu, Ni, Cr and Fe in canned fish are presented in Table.1, figure 1 and figure 2 along with the statistical parameters. Ten samples for each canned fish were analyzed to assess the amounts of these metals.

Table 1: metal contents µg/g in various varieties of canned sardines.

Metals samples	Cu (µg/g) Mean±SD	Ni (µg/g) Mean±SD	Cr (µg/g) Mean±SD	Fe (µg/g) Mean±SD
Yacout sardines(Morocco)	0.7±0.03	0.14±0.043	0.10±0.0332	21±1.685
Marina sardines(Tunisia)	0.9±0.0303	0.12±0.035	0.08±0.02	25±1.1
Silver sardines(Morocco)	2.1±0.367	0.12±0.055	0.10±0.0245	20±1.886
Salsa sardines(China)	1.0±0.41	0.14±0.0285	0.11±0.0274	30±0.831

Data analysis showed significant differences in means of concentrations of Cu in four sardines canned fish, for Yacout sardine the concentration of Cu was lower in magnitude compared to the other canned sardines evaluated in this study, but it can be seen that the average concentration of Cu in Silver sardine is more than 2 times higher than other three types. The data for Ni metal showed no significant differences in means of concentrations among all samples of canned fish, relatively

lower levels of Ni noticed in Marina sardines and silver sardines, wherease, higher levels were in Yacout sardines and Salsa sardines.Similarly the mean of concentrations of Cr showed no significant differences among all samples,the average Cr content in Marina sardines was low as compared to other samples while in Salsa sardines was high. The data showed significant differences in means of Fe concentrations in the various types of canned sardine, it can be seen that the average concentrations of Fe in Salsa sardine is more highly than that in Silver sardines and Yacout sardines, the Fe content in Marina sardines is more than Silver and Yacout sardines but lower than Salsa sardines.

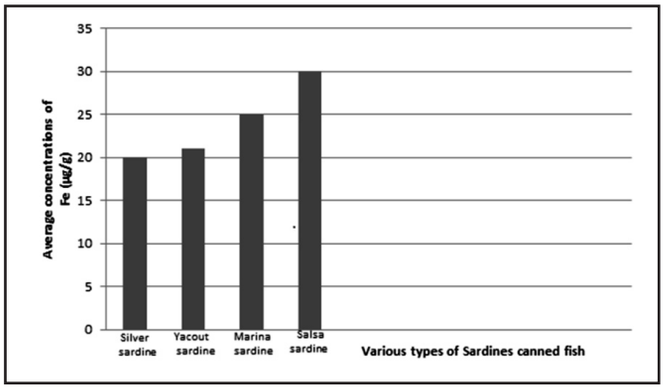

Figure:1. Iron lvels in four tyepes of sardines canned fish.

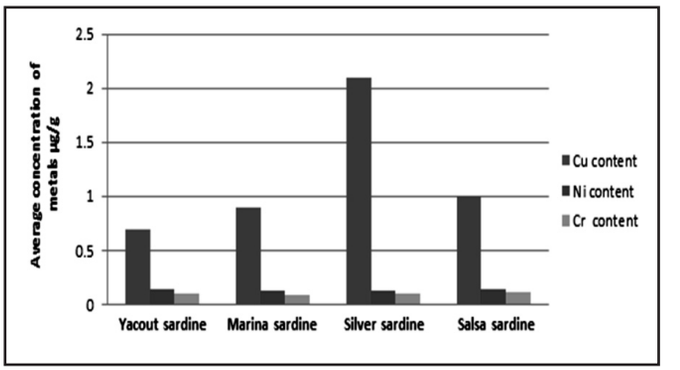

Figure:2. Comparative levels of selected heavy metals in sardines canned fish.

Discussion;

There is increasing concern about the quality of foods in several parts of world. The level of heavy metals in fish depend upon many factors like contaminants in the water, the feeding habits of each fish species, water chemistry and any contamination of fish during processing, also weight of fish and sex(8). The quality of the lacquer coatings canned product ,oxygen concentration in the headspace, the pH of canned product and storage place may control the metal levels in canned fish(11). 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 µg/g can cause adverse health problems such as liver and kidney damage(12). WHO(1996) (13) ,MAFF(1994) (14) and FAO(1983) (15) permit levels up to 30 µg/g. Literature values for canned sardines marketed in Brasilia and in the USA, Cu content have been reported to be between 1.31 and 2.25 (16) and 0.50 - 1.75 µg/g (12) respectively. Likewise, the average amounts of Cu in canned sardines consumed in the Kingdom of Saudi Arabia have been reported as 2.26 µg/g , while 1.96 µg/g were found for Cu in canned sardines in Turkey(4,9), these findings are compatible with current study results and show that Cu in four types canned sardines is well below the recommended limits. Concentrations of Ni in canned sardines from Nigeria,Thailand and Pakistan were 3.11 µg/g ,1.33 µg/g and 0.52 µg/g respectively(17,18).Current study levels of Ni were significantly lower than those reported levels. In literature Ni levels ranged from 0.66 to 1.59 µg/g for muscles of fish from Iskenderun(19),<0.01-2.04 µg/g for muscles of fish from the black sea coast(20),0.02-3.97 µg/g for muscles of fish from the Marmara,Aegean and Mediterranean seas(11). Chromium Cr is essential for human health, Chromium (III) is an essential nutrient that helps the body use sugars, proteins, and fats, but Cr (VI) is carcinogenic (21) the adequate dietary intake in adults can range from 0.50 to 2.00 µg(16). Excessive amount of Cr(III) may cause adverse health effects(22) The World Health Organization (WH O) has proposed that chromium (VI) is a human carcinogen. Several studies have shown that chromium (VI) compounds can increase in risk of lung cancer (23). Animal studies have also shown an increase in risk of cancer (24). In the literature, Cr levels in fish have been reported to be in the range of 0.10-1.60 µg/g for muscles of fish from the Turkish sea(22) 0.06-0.84 µg/g for muscles of fish from the black sea coasts(20),0.31-0.73 µg/g for muscles of fish from the western coast of the United Arab Emirates (25). In the current study Chromium contents were well within the limits prescribed by the FDA. The values were also within the limits of 12– 13µg/ g(26). Iron (Fe) has biological importance. Iron deficiency causes anemia and the fish are major dietary sources for this important nutrient(12). However , it is also known that when the intake of Fe is more than 15.0 µg/g , it can produce toxic effects(9) ,mammals are not able to excrete excess iron, and chronic iron overload is associated with a slowly progressing failure of various organs(27). Levels of Fe in canned fish show a wide variation around the world, the Fe levels in the literature have been reported to be between 4.83-29.2 µg/g in canned sardines marketed in USA and 21.0-88.8 µg/g in canned sardines marketed in Brasilia(12,16). In this study, the average Fe concentrations were 21 µg/g for the samples of Yacout sardines (Morocco), 25 µg/g for Marina sardines(Tunisia), 20 µg/g for Silver sardines(Morocco) and 30 µg/g for Salsa sardine(China), all of which were above the permissible limit (15 µg/g). Therefore, it is clear that the Fe

levels of many canned sardine samples are above the limits recommended.

Conclusion:

The results from this study suggested that some significant differences existed in the metal concentrations across different canned sardine types in Iraq . Also, analytical data obtained from this study shows that the metal concentrations for the varieties of canned sardines except Fe were generally within the U.S.EPA, FAO/WHO, and U.S.FDA recommended limits for canned fish and do not cause any risk for the local consumers due to their low intake. But contamination of Fe in majority of canned sardine samples may cause risk for the consumers. Therefore ,more researches and assessments of canned fish are needed in Iraq to provide more data and help safeguard the health of Iraqi citizens.

Authors' contributions:

Dr .khalid Nssaief Jasim designed the study, acquired the data and reviewed the study.

M.Sc. Samir Laybi shkhaier designed the study, analyzed the data, wrote the article and reviewed the study.

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