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بحوث العدد

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Abstract:

Canned tuna fish is one of the most distributed foods in the Libyan market. There are many kinds of canned tuna fish imported from different countries while others have been canned in the country. The validity of canned tuna fish these kinds and their conformity with the Libyan and the international standards is questionable. This is what leads us to conduct this study in order to find a confirmation or deny of these suspicions. Eight samples of common canned tuna fish in the Libyan market have been chosen to investigate two of the common heavy metals that are widespread in water and many types of food and have negative impacts on human health. Mercury and cadmium have been investigated in 24 repeated samples for each metal to know the concentration of these metals in the samples that have been chosen. The results have revealed that all the kinds of canned tuna contain different amounts of these two metals. In addition, the results reveal that the concentrations of these metals are below the limits that the Libyan and the international standards require.

Key words: canned tuna fish, Heavy metals, Human Health, Standards, Cadmium, Mercury.

Introduction:

Health is everyone's main objective while the nations' wealth is measured by the health of their people. Water, Air, and Food are necessary for lives continuation. In general, we can consider that all hazards which target humans take one of the previous paths in what is known as food contamination. Therefore, food contamination is the existence of microbes or any unwanted objects in food and cause food poisoning. Food contamination takes many forms that make this food unusable or undesirable for human consumption. These forms might be microbial, chemical, or radioactive contamination (Abua et al, 2005). Red and white meats are from the most usable substances because of their containment of many important nutrients such as proteins, essential amino acids, vitamins, and minerals that are needed for growth and the body's natural operations. Fish, which is considered as white meat, with its nutrients is an important food for humans. It is widely consumed in many parts of the world. It is a source of complete proteins, which are easily digested. This source of fish also contains the essential minerals such as phosphorous, magnesium, and calcium. It also contains omega three (Abua et al, 2005). for instance, it carries high content of two kinds of omega three polyunsaturated fatty acids: eicosapentaenoic acid (EPA) and docosahexaenoic acid (DHA) that have protective effects in preventing coronary heart disease. Fish contains some metals such as copper and zinc which are essential in human nutrition and the increase of them over the limits can cause health problems for the short and long terms. In addition, the fish meat contains some other metals such as lead, cadmium, mercury, and arsenic. These metals known as the heavy metals, which are their density more than 5 g/cm^3, do not have any nutrition value, and they are toxic (P. Sivaperumal et al, 2006; M. Al-Busaidi et al, 2011). The danger of these metals comes from their impact on the natural balance and their concentration is magnified through the food chain (Quratulan Ahmed et al, 2015; AyubEbadi Fathabad et al, 2015). These metals considered as dangerous metal contaminants, which carry pathogens satisfactory by one way or other that affect human health and safety. These metals are considered as the most important aquatic contaminants (Ashraf et al, 2006). These metals present in organs and tissues of tuna fish due to the emergence of the industrial and agricultural contamination. This presence accompanies the development in the recent centuries which reach the sea, the natural habitat of the tuna fish (Ebrahim Rahimi et al, 2010; Boadi, et al, 2011). Therefore, many poisoning cases have emerged in many places around the world. Heavy metals are not necessary or valuable for humans but they have negative impact on the metabolism especially with high concentrations. However, all elements might be toxic with high doses. Sometimes it is difficult to distinguish between the toxicity and the lack of the element because the smallness of the difference between them. Also, it is difficult to separate the element toxicity because in reality elements react with each other in varying degrees and according to the functional impact of the metal. For instance, cadmium toxicity depends on the amount of zinc that exists in the body. Iron functions in the cells affected by copper and cobalt and less on zinc. Therefore, it is important to distinguish between essential, nonessential elements, and the most toxic elements. In fact, elements toxicity depends on their concentrations that are in the taken substance (P. Sivaperumal et al, 2006; Al-Busaidi et al, 2011; Quratulan Ahmed et al, 2015). Contamination by heavy metals considers as a dangerous problem because of the trend of these compounds to gather and accumulate inside the living organisms' bodies that live in different ecosystems. The reason behind that is their complicated chemical reactions (M. Safiur Rahman et al, 2002). The technological development accompanies the tremendous use of these compounds make the international organizations care about the limitations of their use and find the ways to get rid of them and control their existence. The most dangerous heavy metals are lead, mercury, arsenic, and cadmium (Voegborlo et al 1999; Mahalakshmi et al 2011). In this study, we will focus on two of them, which are mercury and cadmium because they are the most important heavy metals that find in aquatic systems and have negative impacts on the human health. Cadmium occurs naturally in ores together with zinc, lead, and copper. Cadmium compounds are used as stabilizers in PVC products, color pigments, several alloys and, now most commonly, in re-chargeable nickel–cadmium batteries. Metallic cadmium has mostly been used as an anticorrosion agent (cadmiation). Cadmium is also present as a pollutant in phosphate fertilizers. EU cadmium usage has decreased

considerably during the 1990s, mainly due to the gradual phase-out of cadmium products other than Ni-Cd batteries and the implementation of more stringent EU environmental legislation (Directive 91/338/ECC). Notwithstanding these reductions in Europe, however, cadmium production, consumption, and emissions to the environment worldwide have increased dramatically during the 20th century. Cadmium containing products are rarely re-cycled, but frequently dumped together with household waste, thereby contaminating the environment, especially if the waste is incinerated. Natural as well as anthropogenic sources of cadmium, including industrial emissions and the application of fertilizer and sewage sludge to farm land, may lead to contamination of soils, and to increase cadmium uptake by crops and vegetables, grown for human consumption. The uptake process of soil cadmium by plants is enhanced at low pH (Lars et al, 1998). Cigarette smoking is a major source of cadmium exposure. Biological monitoring of cadmium in the general population has shown that cigarette smoking may cause significant increases in blood cadmium (B-Cd) levels (Nnorom et al 2005). The concentrations in smokers being on average 4–5 times higher than those in non-smokers. Despite the evidence of exposure from environmental tobacco smoke, however, this is probably contributing little to total cadmium body burden. Food is the most important source of cadmium exposure in the general non-smoking population in most countries (Lars Järup, 2003). Cadmium is present in most food types, but concentrations vary greatly, and individual intake also varies considerably due to differences in dietary habits (Lars et al, 1998). Women usually have lower daily cadmium intakes, because of lower energy consumption than men. Gastrointestinal absorption of cadmium may be influenced by nutritional factors, such as iron status (Flanagan et al,1978). B-Cd generally reflects current exposure, but partly also lifetime body burden (Lars et al, 1983). The cadmium concentration in urine (U-Cd) is mainly influenced by the body burden, U-Cd being proportional to the kidney concentration. Smokers and people living in contaminated areas have higher urinary cadmium concentrations, smokers have about twice as high concentrations as non-smokers (Lars et al, 2003).
Inhalation of cadmium fumes or particles can be life threatening. Although acute pulmonary effects and deaths are uncommon, sporadic cases still occur (Seidal et al, 1993; Barbee et al, 1999). Cadmium exposure may cause kidney damage. The first sign of the renal lesion is usually a tubular dysfunction, evidenced by an increased excretion of low molecular weight proteins such as β2-microglobulin and α1-microglobulin (protein HC) or enzymes such as N-Acetyl-β-D-glucosaminidase (NAG) (Lars et al, 2003; Who, 1992). It has been suggested that the tubular damage is reversible (Hotz et al, 1999), but there is overwhelming evidence that the cadmium induced tubular damage is indeed irreversible (Lars et al, 2003). WHO in its 1992 cadmium review estimated that a urinary excretion of 10 nmol/mmol creatinine (corresponding to circa 200 mg Cd/kg kidney cortex) would constitute a ‘critical limit’ below which kidney damage would not occur. However,

WHO calculated that circa 10% of individuals with this kidney concentration would be affected by tubular damage. Several reports have shown that kidney damage and/or bone effects are likely to occur at lower kidney cadmium levels. European studies have shown signs of cadmium induced kidney damage in the general population at urinary cadmium levels around 2–3 μg Cd/g creatinine (Buchet et al, 1990; lars et al, 2000). The initial tubular damage may progress to more severe kidney damage, and already in 1950 it was reported that some cadmium exposed workers had developed decreased glomerular filtration rate (GFR) (Friberg, 1950). This has been confirmed in later studies of occupationally exposed workers (Bernard et al,1992; Lars et al, 1995). An excess risk of kidney stones, possibly related to an increased excretion of calcium in urine following the tubular damage, has been shown in several studies (Lars et al, 2003). Recently, an association between cadmium exposure and chronic renal failure [end stage renal disease (ESRD)] was shown (Hellstrom et al, 2001). Using a registry of patients, who had been treated for uraemia, the investigators found a double risk of ESRD in persons living close to (<2 km) industrial cadmium emitting plants as well as in occupationally exposed workers. Long-term high cadmium exposure may cause skeletal damage, first reported from Japan, where the itai-itai (ouch-ouch) disease (a combination of osteomalacia and osteoporosis) was discovered in the 1950s (Bernard, 2008). The exposure was caused by cadmium-contaminated water used for irrigation of local rice fields. A few studies outside Japan have reported similar findings (Lars et al, 2003). During recent years, new data have emerged suggesting that also relatively low cadmium exposure may give rise to skeletal damage, evidenced by low bone mineral density (osteoporosis) and fractures (Staessen et al, 1999; Alfven et al,2000; Nordberg et al, 2002). Animal experiments have suggested that cadmium may be a risk factor for cardiovascular disease, but studies of humans have not been able to confirm this (Jarup et al, 1998). However, a Japanese study showed an excess risk of cardiovascular mortality in cadmium-exposed persons with signs of tubular kidney damage compared to individuals without kidney damage (Nishijo et al, 1995). The IARC has classified cadmium as a human carcinogen (group I) on the basis of sufficient evidence in both humans and experimental animals (IARC, 1995). IARC, however, noted that the assessment was based on few studies of lung cancer in occupationally exposed populations, often with imperfect exposure data, and without the capability to consider possible confounding by smoking and other associated exposures (such as nickel and arsenic). Cadmium has been associated with prostate cancer (Tabari et al, 2010), but both positive and negative studies have been published. Early data indicated an association between cadmium exposure and kidney cancer (Kolonel, 1976). Later studies have not been able clearly to confirm this, but a large multi-center study showed a (borderline) significant over-all excess risk of renal-cell cancer, although a negative dose–response relationship did not support a causal relation (Mandel et al, 1995). Furthermore, a population-based multicenter-study

of renal cell carcinoma found an excess risk in occupationally exposed persons (Pesch et al, 2000). In summary, the evidence for cadmium as a human carcinogen is rather weak, in particular after oral exposure. Therefore, a classification of cadmium as 'probably carcinogenic to humans' (IARC group 2A) would be more appropriate. This conclusion also complies with the EC classification of some cadmium compounds (Carcinogen Category 2; Annex 1 to the directive 67/548/EEC) (Lars Jarup, 2003).
The mercury compound cinnabar (HgS), was used in pre-historic cave paintings for red colors, and metallic mercury was known in ancient Greece where it (as well as white lead) was used as a cosmetic to lighten the skin. In medicine, apart from the previously mentioned use of mercury as a cure for syphilis, mercury compounds have also been used as diuretics [calomel (Hg2Cl2)], and mercury amalgam is still used for filling teeth in many countries (WHO, 1991). Metallic mercury is used in thermometers, barometers and instruments for measuring blood pressure. A major use of mercury is in the chloralkali industry, in the electrochemical process of manufacturing chlorine, where mercury is used as an electrode. The largest occupational group exposed to mercury is dental care staff. During the 1970s, air concentrations in some dental surgeries reached 20 μg/m3, but since then levels have generally fallen to about one-tenth of those concentrations. Inorganic mercury is converted to organic compounds, such as methyl mercury, which is very stable and accumulates in the food chain. Until the 1970s, methyl mercury was commonly used for control of fungi on seed grain. The general population is primarily exposed to mercury via food, fish being a major source of methyl mercury exposure (WHO, 1990), and dental amalgam. Several experimental studies have shown that mercury vapor is released from amalgam fillings, and that the release rate may increase by chewing (Sallsten et al, 1996). Mercury in urine is primarily related to (relatively recent) exposure to inorganic compounds, whereas blood mercury may be used to identify exposure to methyl mercury. A number of studies have correlated the number of dental amalgam fillings or amalgam surfaces with the mercury content in tissues from human autopsy, as well as in samples of blood, urine and plasma (WHO, 1991). Mercury in hair may be used to estimate long-term exposure, but potential contamination may make interpretation difficult. Health effects Inorganic Mercury. Acute mercury exposure may give rise to lung damage. Chronic poisoning is characterized by neurological and psychological symptoms, such as tremor, changes in personality, restlessness, anxiety, sleep disturbance and depression. The symptoms are reversible after cessation of exposure. Because of the blood–brain barrier there is no central nervous involvement related to inorganic mercury exposure. Metallic mercury may cause kidney damage, which is reversible after exposure has stopped. It has also been possible to detect proteinuria at relatively low levels of occupational exposure. Metallic mercury is an allergen, which may cause contact eczema, and mercury from amalgam fillings may give rise to oral

lichen. It has been feared that mercury in amalgam may cause a variety of symptoms. This so-called ‘amalgam disease’ is, however, controversial, and although some authors claim proof of symptom relief after removal of dental amalgam fillings (Lindh et al, 2002), there is no scientific evidence of this (Langworth et al, 2002). Organic mercury Methyl mercury poisoning has a latency of 1 month or longer after acute exposure, and the main symptoms relate to nervous system damage (Weiss et al, 2002). The earliest symptoms are paresthesia and numbness in the hands and feet. Later, coordination difficulties and concentric constriction of the visual field may develop as well as auditory symptoms. High doses may lead to death, usually 2–4 weeks after onset of symptoms. The Minamata catastrophe in Japan in the 1950s was caused by methyl mercury poisoning from fish contaminated by mercury discharges to the surrounding sea. In the early 1970s, more than 10,000 persons in Iraq were poisoned by eating bread baked from mercury-polluted grain, and several thousand-people died as a consequence of the poisoning. However, the general population does not face significant health risks from methyl mercury exposure with the exception of certain groups with high fish consumption. A high dietary intake of mercury from consumption of fish has been hypothesized to increase the risk of coronary heart disease (Salonen et al, 1995). In a recent case-control study, the joint association of mercury levels in toenail clippings and docosahexaenoic acid levels in adipose tissue with the risk of a first myocardial infarction in men was evaluated (Guallar et al, 2002). Mercury levels in the patients were 15% higher than those in controls (95% CI, 5–25%), and the adjusted odds ratio for myocardial infarction associated with the highest compared with the lowest quintile of mercury was 2.16 (95% CI, 1.09–4.29; P for trend = 0.006). Another recent case-control study investigated the association between mercury levels in toenails and the risk of coronary heart disease among male health professionals with no previous history of cardiovascular disease. Mercury levels were significantly correlated with fish consumption, and the mean mercury level was higher in dentists than in non-dentists. When other risk factors for coronary heart disease had been controlled for, mercury levels were not significantly associated with the risk of coronary heart disease (Yoshizawa et al, 2002). These intriguing contradictory findings need to be followed up by more studies of other similarly exposed populations (Lars Järup, 2003).

In Libya, canned tuna fish is one of the common foods. Companies and traders compete to find a chance and a place in the market to distribute their types that they import from different world countries or produce in their factories in the country.

Materials and Methods:

Sampling:

We collected randomly eight different brands of light solid 200 grams in salt solution and plant oil canned tuna fish with three repeats for each brand from

Khoms, Libya market to investigate two heavy metals which are mercury and cadmium.

Reagents:

- Nitric acid HNO_3 65%.
- De-ionized water H_2O_2 35%.
- Distilled water.

Tools:

-250 ml volumetric flask.

- Litmus paper No 6.

Apparatuses:

- Atomic absorption spectrophotometer (AAS).
- Direct Mercury Instrument (DMI).
- Benzes Burner.
- Thermal condenser.

The chemical analysis:

- Mercury:

0.2 g from each sample was put in crucible and put into DMI then get the reading.

- Cadmium:

Samples preparation and digestion:

- Put 5 g of a sample in 250 ml conical flask.
- Add 10 ml HNO_3 and 5 ml H_2O_2 to the sample and leave it for an hour in a cool place.
- Put the sample for two hours under a condenser with 90 C^o.
- Evaporate the sample to reach 2 ml.
- Leave the sample to cool.
- Filter the sample with No 6-litmus paper.
- Add water to the flask until 25 ml.

The chemical analysis:

Put the samples in AAS and get the reading.

Results and Discussion:

From the chemical analysis, we have gotten the results that are shown in table (1).

Table (1) the average concentration of Hg and Cd in the samples

S. No	Name	Cd ppm	Hg ppm
1	Italian Marlebu	0.1677	0.0757
2	Portuguese	0.2354	0.1991
3	Sun 1 Thailand	0.1410	0.3127
4	skipjack Thailand	0.1963	0.0442

5	Italian	0.1519	0.2942
6	Janzor (Libya)	0.1657	0.0372
7	Omanian	0.1697	0.0311
8	Alwafa (Libya)	0.1324	0.0521

The results of the study of mercury reveal and as shown in table (1) and chart (1) that the highest concentration is 0.31 ppm in sample number (3) and the lowest concentration is 0.03 ppm in sample number (7).

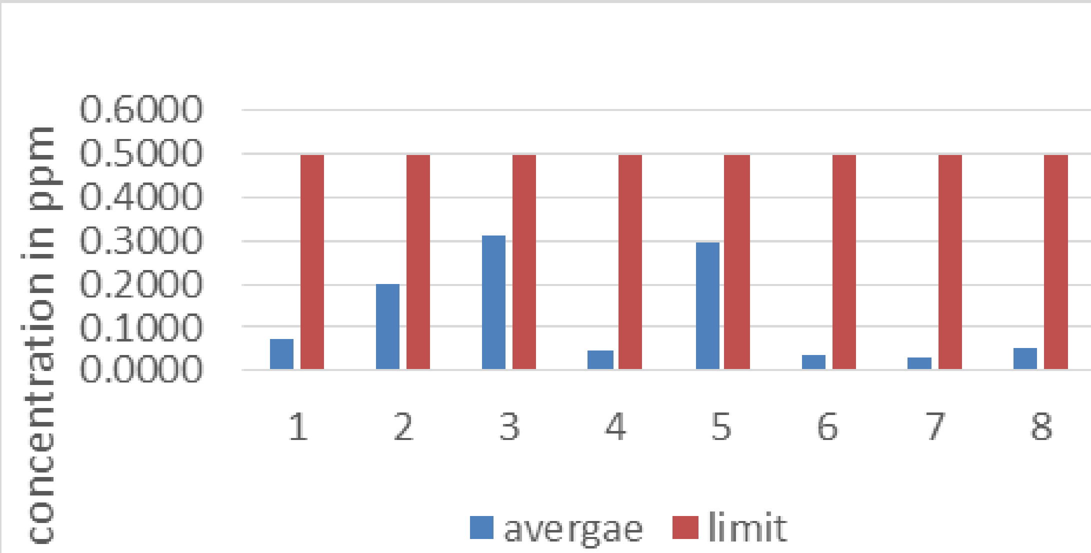

Figure (1) the concentration of mercury in tuna studied samples and their comparsion to the standards

The results of cadmium reveal as shown in table (1) and chart (2) that sample (2) is the highest concentration with 0.23 ppm and sample (8) is the lowest concentration with 0.13 ppm.

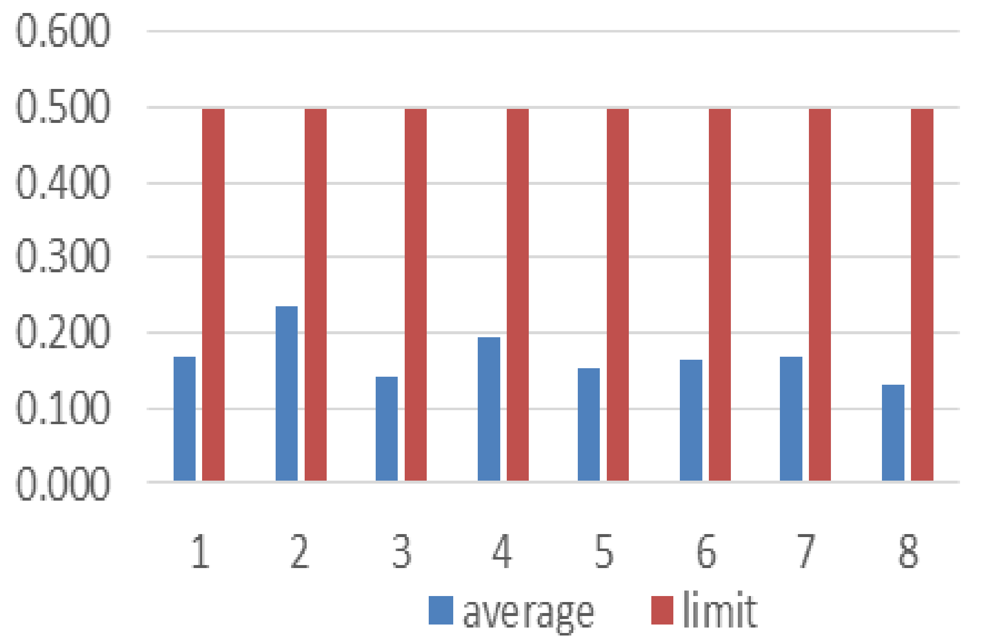

Figure (2) the concentration of cadmium in tuna studied samples and their comparsion to the standards

Discussion:

From the results, all the samples contain amounts of mercury and cadmium. These amounts are under the concentration limits of mercury and cadmium as the Libyan and the international standards. However, the concentrations of these heavy metals can cause problems to the consumers in the long run because of the bioaccumulation properties of these metals. These metals and from the continual use of the contaminated source such as the tuna fish accumulated in the human bodies to reach the effective levels. Whole finfishes in general contain Cd 0.1 - 0.3 mg/kg ww, whereas fish muscle usually contains Cd less than 0.1 mg/kg ww and fish liver Cd concentration is greater and reaches up to 24.7 mg mg/kg ww (Eisler, 2010). High Cd concentration in the water sediments is reflected in Cd content of prey (Eisler, 2010). To safeguard human consumers of tuna fish, the European Union recommends less than 0.1 mg/kg ww; the same level of protection is recommended in Turkey, and China (European-Commission, 2006; Eisler, 2010). Regular monitoring the Hg contamination in fish and fishery products is essential to protect vulnerable population such as children (Yang et al, 2015). The Hg body burden in fishes caught off Atlantic Ocean is higher than conspecific species of equal size caught off Mediterranean Sea. It is possible that the higher Hg body burdens were due to the greater natural geochemical Hg levels in the Mediterranean Sea (Eisler, 2010). Data on Hg accumulations in several types of tuna fish are particularly abundant. The variation in Hg concentration in tuna represents a critical point during risk analysis for consumers (Storelli et al, 2010). Elevated Hg levels can be harmful, especially if excess quantities of tuna are consumed by pregnant women and young children, as bioaccumulation of Hg can damage the developing brain of a fetus or a child (Bratt, 2010). Geographical areas of concern where Hg concentrations in marine fish muscle exceed current regulations for human consumers include Italy, Spain, Taiwan, Florida, and Oregon (Eisler, 2010). After different culinary treatments, no significant Hg loss was observed for uncooked and boiled fish. However, 4 to 25% Hg loss was observed in yellowfin tuna after roasting (175 °C for 20 min) or frying (180 °C for 5 min) (Schmidt et al, 2015). Canned tuna fish from the Mediterranean coast of Libya had Hg levels. Current study revealed that Hg had the highest concentrations among tested trace elements, followed by Pb and Cd either in fresh little tunny or canned skipjack and yellowfin tuna. This order of measured trace elements concentrations is in agreement with occurrence of such toxic metals in Italian fresh and canned tuna (Storelli et al, 2010). On the other hand, Cd and Pb concentrations either in fresh little tunny caught off Libya or canned tuna sold in Tripoli city did not surpass the toxicological standard levels (European- Commission, 2006), and accordingly there was minor food safety concerns of Cd or Pb toxicity from eating tuna therein. Different amounts of Cd, Hg in the samples. Hg from 0.03 ppm in the Omanian tuna to 0.31 ppm in Sun 1 Thailand. This indicates that the concentration of Hg under Libyan and international limits which put 0.5 ppm as the maximum safe concentration of this metal in tuna fish that used for human food. The other brands have different amounts of this metal. For example, the two Italian brands contain different amounts. Marlebu contains 0.0757 ppm and Italian contains 0.2942 ppm. This means that every source has different characteristics and one country of importation can deliver different food qualities. This probability indicates that the Italian brand uses tuna fish from out the Mediterranean Sea which according to Abolghait (2015) that Hg body burden in fishes caught off Atlantic Ocean is higher than that which caught off Mediterranean Sea. Canned tuna fish from the Mediterranean coast of Libya has Hg levels well below the permissible limits at range from 0.20 to 0.66 with an average value of 0.29 mg/kg ww. (Voegborlo et al, 1999).

Cd concentration results from 0.1324 ppm in Alwafa brand to 0.2354 ppm in Portuguese brand. This also indicates that all the brands burden under Libyan and international limits. As in Hg, Cd is different in brands that import from the same country. For example, Sun 1 and Skipjak from Thailand have different concentration of Cd. Sun 1 has 0.1410 ppm while Skipjak has a concentration of 0.1963 ppm. This indicates that different brands have different sources of fish which has different burden of Cd.

The other important issue related to canned tuna fish is the human daily intake of these metals with this tuna fish. The daily intake plays a big role in heavy metal bioaccumulation and bio magnification in human bodies and the appearance of toxicity in these bodies because most of the fish that eaten by public comes from commercial sources. This issue needs more focus and investigation by scientists and researchers to identify the influence of these brands and many others that are distributed in the Libyan market and highly consumed in the daily meals and dishes by the majority of the residents in the country.

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الفهـــــــــرس

يشترط في البحوث العلمية المقدمة للنشر أن يراعى فيها ما يأتي :

- أصول البحث العلمي وقواعده .
- ألا تكون المادة العلمية قد سبق نشرها أو كانت جزءا من رسالة علمية .
- يرفق بالبحث تزكية لغوية وفق أنموذج معد .
- تعدل البحوث المقبولة وتصحح وفق ما يراه المحكمون .
- التزام الباحث بالضوابط التي وضعتها المجلة من عدد الصفحات ، ونوع الخط ورقمه ، والفترات الزمنية الممنوحة للتعديل ، وما يستجد من ضوابط تضعها المجلة مستقبلا .

تنبيهات :

- للمجلة الحق في تعديل البحث أو طلب تعديله أو رفضه .
- يخضع البحث في النشر لأولويات المجلة وسياستها .
- البحوث المنشورة تعبر عن وجهة نظر أصحابها ، ولا تعبر عن وجهة نظر المجلة .

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