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Determination of Cu, Co, and Pb in selected frozen fish tissues collected from Benghazi markets in Libya

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ABSTRACT

The concentrations of some heavy metals (Cu, Co, and Pb) were investigated in muscle, liver and gills of three fish species (Mullus surmuletus, Seriola dumerili, and Sparus aurata) collected from frozen fish markets in Benghazi city, Libya, during winter 2016, using flame atomic absorption spectrometry (FAAS). The mean concentrations (μg/g) of the heavy metals in fish tissues ranged as follows: Cu (44.80 – 79.33), Co (198.66 – 238.26), Pb (56 – 192). The highest mean concentration, 238.26μg/g was recorded for Co in the muscle of Mullus surmuletus, on the other, the lowest mean concentration, 44.80 μg/g, was recorded for Cu in gills of Mullus surmuletus. The concentrations for Cu and Pb in all fish samples were over the Effect Range-Low (ERL) but were under the Effect Range-Median (ERM) in metal pollution index (MPI). The concentrations of (Cu, Co and Pb) were higher than the maximum permissible limits specified by some food regulatory bodies like WHO. The results indicate that heavy consumption of frozen fishes in Benghazi city markets may pose a health risk to the consumers.

Graphical Abstract

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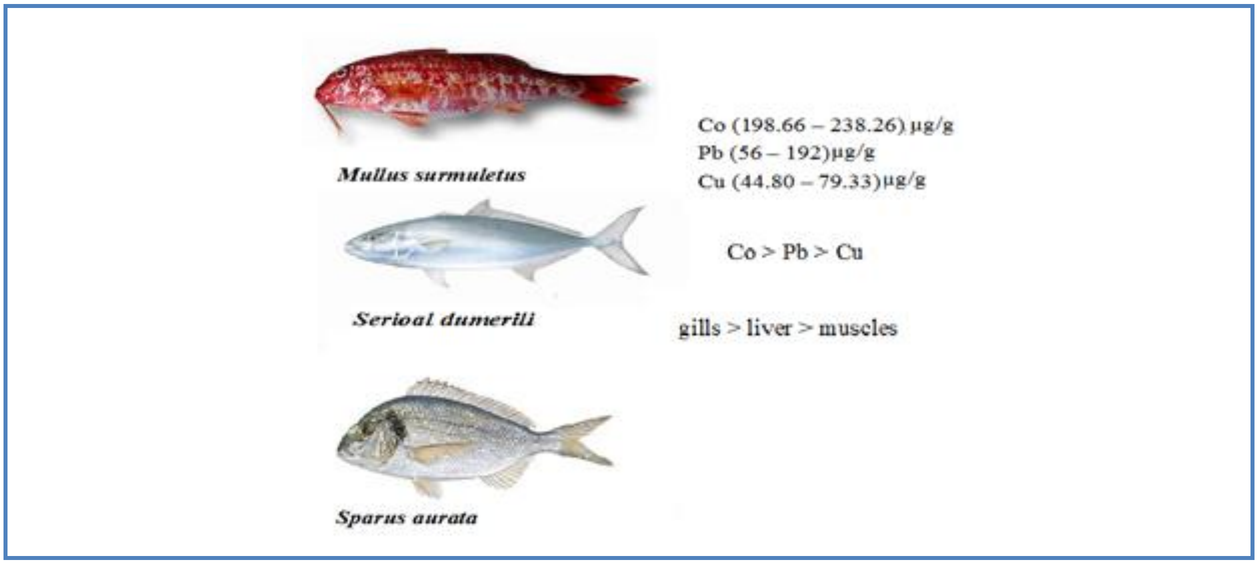

Introduction

The term heavy metals is a general collective term which can be applied to a group of metals and metalloids with atomic density greater than 4g/cm3 or 5 times or more greater than water [1]. Depending upon their concentration, they may exert beneficial or harmful effects on plant, animal and human life [2]. Some of these metals are toxic to living organisms even at low concentrations, whereas others are biologically essential and become toxic at relatively high concentrations. When ingested in excess amounts, heavy metals combine with body's bio-molecules like proteins and enzymes in order to form stable bio-toxic compounds, thereby mutilating their structures and hindering them from the bio-reactions of their functions [1].

The toxicity of metals depends on the metal type and concentration, the period of exposure and other factors. Also, metals join in the food chain and are responsible for adverse effects and death in the aquatic organisms [3].

During recent decades, contamination of aquatic systems by heavy metals has become a global problem. Heavy metals may enter aquatic systems from different natural and anthropogenic (human activities) sources including industrial or domestic wastewater, application of pesticides and inorganic fertilizers, storm runoff, mineral leaching from landfills, shipping and harbor activities, geological weathering of the earth crust and atmospheric deposition [4].

Accumulation of pollutants in the environment has always been an issue of concern to scientists [5]. Heavy metals, unlike organic pollutants, cannot be chemically degraded or biodegraded by microorganisms. Thus, their content has steadily increased in soils and subsequently accumulated in plants, animals, and even in humans [6]. Marine organisms are characterized by a greater spatial ability to accumulate metals compared to bottom sediments, for this reason, fishes are widely used as bio-indicator for aquatic or marine pollution by metals and have also been used to evaluate ecological risk [7-10].

Fish is at the top of the aquatic food chain and normal metabolism of fish may accumulate large amounts of certain metals from water, food and sediment. Thus, like essential metals, non-essential metals are also taken in by fish and accumulate in the tissue. Studies from the field and laboratory experiments show that accumulation of heavy metals in the tissue depends on metal concentration in water and exposure period beside the fact that some environmental factors such as salinity, pH, hardness and temperature play a significant role in metal accumulation. Ecological needs, sex, size, seasonal changes and molt of marine animals were also found to affect metal accumulation in their tissue [11].

The main aim of this study can be summarized in the following points:

- Estimation of some heavy metals (Cu, Co, and Pb) in muscle, liver and gill tissues.

-To find out whether or not the fish from the local market have elevated concentrations of these heavy metals in their tissues as being dangerous for human consumption.

Experimental

The mentioned fish species have been collected from markets of frozen fish in Benghazi city, Libya, during winter 2016. The fish samples include (Mullus surmuletus, Seriola dumerili, and Sparus aurata). The fish samples were placed immediately in poly-ethylene bags, put into isolated container of polystyrene ice box and then transferred to the laboratory.

sample preparation:

De-ionized water was used to prepare all aqueous solutions. All plastic and glassware were rinsed and soaked in 10% (v/v) HNO3 overnight. Nitric acid, HNO3, was of highest quality from Merck, Germany.

Before analysis, the fish muscle, liver, and gills tissues of each species were taken using stainless steel instruments on a clean glass working surfaces. 0.25g of each tissue were accurately weighed using electronic balance Model AAA Adam and, then, transferred into 250cm^3 Pyrex conical flask. To each sample, 5ml of concentrated nitric acid (HNO3) were added into the samples and heated on a hot plate in a fume hood. The mixture was heated until a white fume was observed which meant that the digestion was complete.

Determination of Heavy Metals:

After the digestion, the sample was allowed to cool at room temperature and 20 cm3 of distilled water was added to bring the metals into solution. Sample was allowed to cool at room temperature, was filtered using "Whatman" filter paper into a 100 cm3 volumetric flask and made to mark with distilled water. The prepared samples were then transferred into separate plastic bottles, labelled and measured using Perkin Elmer (2380 - USA) Flame Atomic Absorption instrument with acetylene-air flame which was used to detect the heavy metals according to manufacturer conditions. The concentrations of heavy metals were expressed as μg/g for fish organs.

Data Analysis:

Metal Pollution Index (MPI):

Metal pollution index (MPI) was calculated in order to determine overall trace elements concentrations in the analyzed samples. This index calculate the geometrical mean of concentrations of all the metals in different foodstuff [12].

MPI(μg/g) = (Cf1 x Cf2x … xCfn)1/n

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Where Cfn = concentration of n metals in the sample.

All statistical calculations were performed using SPSS 11.0 for Windows. Microsoft Excel (2010) was used to calculate mean and standard deviation and also to plot graphs.

Results and Discussion

The concentration of heavy metals in the various parts of the fish samples as well as mean concentrations, ranges and standard deviations are given in Tables 1 – 3.

The concentration of copper in the three organs under investigation for the selected species illustrated in Tables (1). The concentrations of copper in the organs of Mullus were 61.86, 44.8 and 54.53μg/g in the muscles, liver and gills respectively. While in Seriola fishes sample, the copper concentrations were 69.20, 74.66 and 73.60μg/g in the muscles, liver and gills respectively. On other side, the copper concentrations in Sparus fishes were 73.33, 76.20 and 79.33 μg/g in the muscles, liver and gills respectively. In most species, gills are the second organ which accumulate copper as shown in table (1). It is observed that Sparus and Seriola have the highest concentrations in liver and gills content. This can be related to the species food habit. Tulasi et al., Dural et al., and Ploetz et al., [13-15] reported highest levels of Cu in the liver and gills of some fish species. The higher levels of trace elements in liver relative to other tissues were attributed to the affinity or strong coordination of metallothionein protein with these elements [16]. According to WHO guide lines [17], the allowable concentration of copper for human consumption is 30 μg/g. But the results show that the concentration of copper in all studied tissues are higher than the acceptable safety ranges.

Compared to other heavy metals determined for all studied samples, Co showed high concentration level in the different organs in fish whereas highest means of Co in the present study were found in muscles of Mullus (238.26 μg/g). In other species (Seriola and Sparus), gills are the first organ which accumulated cobalt as shown in table (2), while in Mullus recorded the highest concentration in the muscles. Cobalt is an essential metal as a component of vitamin B12; it is found in most tissues. According to WHO reports, the estimated intake from food is 5–40 μg/day [18], thus from the present data the studied fish have more concentrations than these levels.

Lead concentrations which were ranged between 53.33 and 192 μg/g are higher than the ERL (46.7 μg/g) in all species tissue. Lead was the second accumulated metal in tissues after Cobalt. The highest concentrations of lead were found in muscle followed by gills in most studied samples. Gills which are considered as hard tissues have high value of lead but still lower than the muscles tissues. The high content of lead in gills was attributed to the possibility of particulate or organic lead adsorbed by gills. Lower pH at the gill surface due to respired CO2 may convert lead to a soluble form which could diffuse into the gill tissue. This means that the lead is more accumulated in hard tissues as gills in soft tissues. The level of lead in gills recorded for different species can be arranged in decreasing order as following: Mullus> Sparus> seriola. Generally, these differences in order of Pb are due to the exposure of gills to many external factors like pH, dissolved oxygen and salinity.

WHO recommended that a maximum intake of 3mg/person/week, for children and infants who are more susceptible than adults to lead poising should have intake of less than 1 mg Pb/week. The intelligence of children is being lower in urban areas in which there are high inputs of lead from motor vehicles [19]. The obtained results exhibited high levels of metals comparing to the allowable levels. The concentrations of lead recorded in the fish species under this investigation were greater than the maximum recommended limits of 2.0 μg/g [18-20] in fish food.

Table (1): Cu concentrations (µg/g) in different tissues in fish species

Fish name	Muscle	Liver	Gill
Mullus	61.86	44.80	54.53
Seriola	69.20	74.66	73.60
Sparus	73.33	76.20	79.33

Table (2): Co concentrations (µg/g) in different tissues in fish species

Fish name	Muscle	Liver	Gill
Mullus	238.26	224.53	226.13
Seriola	198.66	203.20	204
Sparus	207.86	212.80	225.60

Table(3): Pb concentrations (µg/g) in different tissues in fish species

Fish name	Muscle	Liver	Gill
Mullus	192	149.33	142.66
Seriola	68	96	92
Sparus	56	70	120

Metal Pollution Index:

MPI is used to compare the total metals accumulation level in various tissues of different fish. MPI values are given in table (4).

Table (4): Metal pollution index calculated for heavy metals concentrations µg/g

Fish name	Tissue	MPI
Mullus	Muscle	141.44
	Liver	114.52
	Gill	120.72
Seriola	Muscle	97.78
	Liver	113.35
	Gill	111.37
Sparus	Muscle	94.86
	Liver	104.31
	Gill	129.02

In Mullus species, MPI were higher in muscles and lower in liver and gills, while in Seriola MPI were higher in liver and lower in gills and muscles. On the other side, in Sparus, the higher MPI were gills. This difference is related to the different feeding habits of fish and the different abilities of fish organs to bind heavy metals [20].

Conclusion:

Among the three fish species, higher concentrations of heavy metals were found in gills of ***Sparus aurata*** in contradiction to the lower concentrations of heavy metals which were also found in muscle of ***Sparus aurata***. Heavy metal concentrations in the organs of fish species follows the order Co > Pb > Cu and their distribution in the organs follow the pattern gills > liver > muscles. The concentrations of Cu, Co and Pb in all the fish samples were above the respective recommended maximum limits.

The metal pollution index (MPI) has been calculated and the results for most studied indicated that fish fluctuated between the calculated MPI for ERL and ERM. However, MPI recorded for gills showed the highest value over other organs in the ***Sparus***, while in ***Seriola*** the highest value for MPI recorded in liver, on the other side, the highest value for ***Mullus*** recorded in muscle. Regarding the mean concentration of the most heavy metal concentration for each metal, it can be said that the concentrations in the samples are generally greater than the recommended maximum limits, hence the samples are not safe for human consumption.

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