



Short Communication

Bioaccumulation of some heavy metals in Red mullet (*Mullus barbatus*), and common Pandora (*Pagellus erythrinus*) from Zliten coast, Libya

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Abstract

This study aimed to determine the heavy metals concentration such as copper (Cu), zinc (Zn), lead (Pb), cadmium (Cd), and mercury (Hg) in the liver, gills, gonad, and muscles of red mullet (*Mullus barbatus*) and Common pandora (*Pagellus erythrinus*) collected in Zliten Coast, Libya. The levels of heavy metals were determined by using an Atomic Absorption Spectrophotometer (AAS). The results showed that the concentration of heavy metals in the sampled fishes was less than the permissible limits for human consumption. In addition, the bioaccumulation for Cu, Pb, Cd, and Hg by both fish species went higher from liver to gills, gonads, muscles respectively, while Zn follows the sequence from gonads, liver, gills, muscles respectively. Therefore, the conclusion of this study was concentrations of heavy metals in the muscle tissue were within the acceptable limits for human health according to FAO and WHO.

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1. Introduction

Seafood has essential amino acids, fatty acids, protein, carbohydrates, vitamins, and minerals. Among kinds of seafood, fishes are widely consumed by people because they have high protein content, low saturated fat, and also omega fatty acids which function to support good health (Ikem and Egiebor, 2005). Fish production in Libya is growing up, and fish consumption by Libyan people is increasing due to its nutritional value and cheapest price. Moreover, the Mediterranean Sea is the main source of production.

The Mediterranean Sea is a semi-enclosed sea which covers 2.5 million km². Human activities such as oil exploration, exploitation, and transportation in the region surrounding the Mediterranean Sea produce a strong environmental impact. In addition, it is also adversely affected by discharges of domestic sewage, industrial, and agricultural wastes. All of these have produced a high concentration polluted environmental of Sea which often reach the maximum global levels (Meadows, 1992) and is compounded by the very slow exchange in Mediterranean water (El-Moselhy and Hamed, 2006). The effective pollutants of heavy metals are considered as the most important pollutants of the aquatic environment because of their toxicity, long persistence, bioaccumulation, and non-biodegradable properties in the food chain (Zyadah and Chouikhi, 1999; Uysal *et al.*, 2008).

Heavy metals such as copper and zinc are essential metals which play an important role in a biological system, whereas mercury, lead, and cadmium are non-essential metals as they are toxic and very harmful elements even at low concentration when having ingested over a long time period. The essential metals can also produce toxic effects when the metal intake is excessively elevated (Turkmen *et al.*, 2008; Tuzen, 2009). Heavy metals may go into fish bodies through the body surface, the gills, or the digestive tract. The gills are regarded as the important site for direct uptake from the water, whereas the body surface is generally assumed to play a minor role in heavy metal uptake in fish. Food may also be an important source for heavy metal accumulation (Obasohan, 2007; Turkmen *et al.*, 2008; Retief *et al.*, 2009). Fish is the final chain of the aquatic food web and an important food source for human. Therefore, heavy metals in aquatic environments are transferred through the food chain into human. Puel *et al.* (1987) reported that heavy metals had the tendency to accumulate in various organs of marine organisms, especially fish, which in turn may enter into the human metabolism through consumption, causing serious health hazards.

For this reason, the determination of heavy metals levels of fish is very important for human health.

In Libya, there are most commercial on two fish species consumed which are Red mullet (*Mullus Barbatus*) and Common pandora (*Pagellus Erythrinus*). The levels of heavy metals were determined in the muscles of Red mullet (*Mullus barbatus*) from the eastern Aegean Sea (Turkey) by Kucuksezgin *et al.* (2001) and Turkmen *et al.* (2005) and in the muscles of Pandora (*Pagellus erythrinus*) from Izmir Bay (Turkey) by Kucuksezgin *et al.* (2002). Whereas, there is limited information on the heavy metal content of fish from the Libyan water. Therefore, the aim of this study was to determine some metal levels (Cu, Zn, Pb, Cd, and Hg) in muscles, livers, gills and gonads from the more popular fish species such as Common pandora (*Pagellus erythrinus*) and Red mullet (*Mullus barbatus*) in Zliten region and to assess whether they are acceptable for human consumption. They also have commercial importance and are considered as one of the most important sources of food in the studied area (Zliten city).

2. Materials and Methods

2.1 Fish Collection

Fresh samples of two fish species were used in this study: Common pandora (*Pagellus erythrinus*) and Red mullet (*Mullus barbatus*). These species are commonly consumed by the local population in Libya.

2.2 Methods

Fish samples were purchased from local fishermen at Zliten harbors (Figure 1) in the same day of capture and brought to the laboratory by an icebox immediately and then frozen at 20°C until dissection. Ten samples from each fish species were obtained. After defrosting, total fish length and weight of the samples were measured in millimeter and gram. Furthermore, they were dissected by using stainless steel dissection instruments whilst wearing surgical gloves. The procedure used for measuring concentrations of heavy metals in tissues has been described previously by Bahnasawy *et al.* (2010).

In order to minimize contamination, all glassware used in the experiment were previously soaked in a soap solution, rinsed in distilled water, acid-washed in dilute HCL, and rinsed in distilled water once again. In addition to this, the chemical used for sample dissolution was all of the analytical grade. Parts (about 1 g) of muscles (epi-axial muscle which was removed from below the dorsal fin of each fish), liver, gills, and gonad were put into small Erlenmeyer flasks and dried in an oven at 105°C

for about 24 hours. In order to determine the percentage of moisture for each sample, the wet and dry masses of the samples were recorded.



Figure 1. Map showing the sampling site (Zlitan coast)

The samples were digested by adding concentrated nitric acid (65%) and per chloric acid (70%) in a 2:1 ratio to the dried samples. Digestion was performed on a hotplate at 200 to 250°C until the solution became clear. The completely digested samples were allowed to cool in room temperature, filtered through an acid-resistant 0.45 µm filter paper, diluted to 25 ml in volumetric flasks with distilled water, and stored in pre-washed glass bottles until the concentration of the metals could be determined. Concentrations of five heavy metals (Cu, Zn, Pb, Cd, and Hg) were measured by using Atomic Absorption Spectrophotometer (NOV AA 400). Metal concentration in tissue was presented as µg metal/g wet weight (µg/g w.w. or ppm).

2.3 Statistical Analysis

Statistical analysis of the obtained data was carried out by using SPSS statistical. One way analysis of variance (ANOVA) was used to identify whether heavy metal concentrations varied significantly. A P value of less than 0.05 was considered to indicate statistical significance.

3. Results and Discussion

The amount of bioaccumulation of heavy metals in tissues may vary depending on the length and weight of samples (Yilmaz, 2005). The average length and weight values of the examined two fish species (*P. erythrinus* and *M. barbatus*) (Table 1).

Average and standard deviations of concentrations

from Cu, Zn, Pb, Cd, and Hg in the liver, gills, gonads, and muscles of the fishes examined *Pagellus erythrinus* and *Mullus barbatus* (Table 2). The contents of investigated heavy metals in fish species were found in the range of 0.18-1.89 ppm for copper, 4.907-41.492 ppm for zinc, 0.125-0.64 ppm for lead, 0.040-0.446 ppm for cadmium, and 0.064-0.432 ppm for mercury. The general order of bioaccumulation for Cu, Pb, Cd, and Hg by both fish species was liver, gills, gonads, and muscles went higher respectively, whereas Zn followed the sequence of gonads, liver, gills, and muscles went higher respectively.

Cu concentrations varied significantly ($P < 0.001$) in both the investigated fishes and the organs of fishes (Table 2). *M. barbatus* contained the higher level of Cu (1.162 ppm) than *P. erythrinus* (0.92 ± 0.63 ppm). The maximum contain of Cu was observed in the liver of *M. barbatus*, while the minimum level was recorded in the muscles of *P. erythrinus*. The maximum Cu level permitted for fish is 20 µg/g for WHO (1993). Copper level in the analyzed fish samples were found to be lower than legal limits.

Zn concentrations varied significantly in both fishes and the organs of these fishes (Table 2). *M. barbatus* accumulated the highest concentration of Zn (24.950 ppm). The gonads were the major sites of Zn accumulation in both fish species containing the highest level of this metal, while muscles had the lowest concentration of it. The maximum zinc level permitted for fish is 100 µg/g according to WHO (1993). Zinc levels in the analyzed fish samples were found to be lower than the legal limits.

Pb concentrations varied significantly in both fishes and the organs of these fishes (Table 2). The highest Pb accumulation (0.43 ppm) was recorded in *M. barbatus*. The liver had the maximum concentration of Pb (0.64 ppm), while muscles contained the minimum concentration (0.12 ppm) in *P. erythrinus*. The maximum lead level permitted for fishes is 2.0 µg/g according to WHO (1993). Lead levels in the analyzed fish samples were found to be lower than the legal recommended limits

Cd concentration varied significantly in both the fishes and the organs of these fishes (Table 2). *M. barbatus* accumulated the highest level of Cd (0.232 ppm). The liver had the highest concentration of Cd while muscle contained the lowest level of it. The maximum cadmium level permitted for fish samples is 0.5 µg/g according to WHO (1993). Cadmium levels in the analyzed fish samples were found to be lower than legal limits.

Table 1. Mean weights and lengths of the species examined in the study (Mean \pm SD).

Parameter	Pagellus erythrinus		Mullus barbatus	
	Range	Mean \pm SD	Range	Mean \pm SD
Total length (cm)	15.5-24.5	18.48 \pm 3.37	14.5-18.0	16.36 \pm 1.38
Total weight (gm)	46.2-175.5	88.47 \pm 48.63	22.3-44.3	32.16 \pm 8.07

Table 2. The mean metals concentrations (ppm) \pm standard division in liver, gills, gonad and muscles of investigated fishes.

Fishes	Mean \pm SD of Copper			
	Liver	Gills	Gonad	Total
<i>P. erythrinus</i>	1.56 \pm 0.57	1.07 \pm 0.34	0.85 \pm 0.41	0.92 \pm 0.63
<i>M. barbatus</i>	1.89 \pm 0.68	1.29 \pm 0.43	1.19 \pm 0.40	1.16 \pm 0.73
Fishes	Mean \pm SD of Zinc			
	Liver	Gills	Gonad	Total
<i>P. erythrinus</i>	14.92 \pm 2.45	17.34 \pm 2.57	29.18 \pm 9.81	16.59 \pm 10.08
<i>M. barbatus</i>	25.27 \pm 4.61	27.13 \pm 4.37	41.49 \pm 9.11	24.95 \pm 13.94
Fishes	Mean \pm SD of Lead			
	Liver	Gills	Gonad	Total
<i>P. erythrinus</i>	0.53 \pm 0.12	0.47 \pm 0.25	0.22 \pm 0.06	0.34 \pm 0.22
<i>M. barbatus</i>	0.64 \pm 0.21	0.50 \pm 0.09	0.37 \pm 0.09	0.43 \pm 0.21
Fishes	Mean \pm SD of Cadmium			
	Liver	Gills	Gonad	Total
<i>P. erythrinus</i>	0.14 \pm 0.02	0.13 \pm 0.05	0.09 \pm 0.03	0.10 \pm 0.04
<i>M. barbatus</i>	0.44 \pm 0.13	0.22 \pm 0.09	0.19 \pm 0.05	0.23 \pm 0.16
Fishes	Mean \pm SD of Mercury			
	Liver	Gills	Gonad	Total
<i>P. erythrinus</i>	0.26 \pm 0.06	0.22 \pm 0.05	0.14 \pm 0.02	0.17 \pm 0.8
<i>M. barbatus</i>	0.31 \pm 0.14	0.43 \pm 0.12	0.28 \pm 0.12	0.27 \pm 0.16

Table 3. Heavy metals concentrations in the organs of *Pagellus erythrinus*

Organs	Liver	Gills	Gonad	Muscles	Total
Element	Mean \pm SD	Mean \pm SD	Mean \pm SD	Mean \pm SD	Mean SD
Cu	1.56 \pm 0.57	1.07 \pm 0.34	0.85 \pm 0.41	0.18 \pm 0.06	0.92 \pm 0.63
Zn	14.92 \pm 2.45	17.34 \pm 2.57	29.18 \pm 9.81	4.91 \pm 0.56	16.59 \pm 10.08
Pb	0.53 \pm 0.12	0.47 \pm 0.25	0.22 \pm 0.06	0.12 \pm 0.03	0.34 \pm 0.22
Cd	0.14 \pm 0.02	0.13 \pm 0.05	0.09 \pm 0.03	0.04 \pm 0.01	0.10 \pm 0.04
Hg	0.26 \pm 0.06	0.22 \pm 0.05	0.14 \pm 0.02	0.06 \pm 0.01	0.17 \pm 0.8

Table 4. Heavy metals concentrations in the organs of *Mullus barbatus*

Organs Element	Liver	Gills	Gonad	Muscles	Total
	Mean \pm SD	Mean \pm SD	Mean \pm SD	Mean \pm SD	Mean SD
Cu	1.89 \pm 0.68	1.29 \pm 0.43	1.19 \pm 0.40	0.27 \pm 0.06	1.16 \pm 0.73
Zn	25.27 \pm 4.61	27.13 \pm 4.37	41.49 \pm 9.11	5.90 \pm 1.92	24.95 \pm 13.94
Pb	0.64 \pm 0.21	0.50 \pm 0.09	0.37 \pm 0.09	0.19 \pm 0.05	0.43 \pm 0.21
Cd	0.44 \pm 0.13	0.22 \pm 0.09	0.19 \pm 0.05	0.06 \pm 0.05	0.23 \pm 0.16
Hg	0.31 \pm 0.14	0.43 \pm 0.12	0.28 \pm 0.12	0.07 \pm 0.02	0.27 \pm 0.16

Table 5. Maximum permissible limits of heavy metals in fish according to international standards

Heavy Metals	Pagellus erythrinus	Mullus barbatus	WHO (1993)	FAO (2009)
	Cu	0.92 \pm 0.63	1.16 \pm 0.73	20 μ g /g
Zn	16.59 \pm 10.08	24.95 \pm 13.94	100 μ g /g	30
Pb	0.34 \pm 0.22	0.43 \pm 0.21	2.0 μ g /g	0.5
Cd	0.10 \pm 0.04	0.23 \pm 0.16	0.5 μ g /g	1
Hg	0.17 \pm 0.8	0.27 \pm 0.16	0.5 μ g /g	0.5

Hg concentration varied significantly in both the investigated fishes and the organs of these fishes (Table 2). *M. barbatus* accumulated the highest level of Hg (0.27 ppm). The gills had the highest concentration of Hg while muscle contained the lowest level of both species. The maximum mercury level permitted for fish is 0.5 μ g/g according to WHO (1993) and FAO (2007). Mercury and cadmium levels in the analyzed fish samples were found to be lower than legal limits.

Heavy metals concentrations in the organs of *P. erythrinus* and *M. barbatus* were also varied (Table 3 & 4). The distribution of metals in the fish organs took the following descending order Zn, Cu, Pb, Hg, Cd respectively. The total concentration values of Cu, Pb, Cd, and Hg in the fish organs were detected in the following order which went higher respectively liver, gills, gonads, and muscles. The sequence of Zn concentration in the organs follow the order which went higher respectively gonads, gills, liver, and muscles. The gonad has been reported as a structure likely to present Zn high concentration due to their participation in excretion of toxic metals, fertilization, cellular division, and growth processes (Mormede and Davies, 2001; Uluturhan and Kucuksezgin, 2007).

In this study, the average concentrations of both

essential and non-essential metals in the liver, gills, gonads, and muscles of each fish species showed significant variations. Statistical analysis revealed that metal concentrations were significantly different in each tissue from different fish species. The differences in the levels of accumulation in the different organs i.e., tissues of a fish could primarily be attributed to the differences in the physiological role of each organ. Regulatory ability, behavior, and feeding habits were other factors which could influence the accumulation differences in the different organs (Kotze *et al.*, 1999). It was also reported that the differences in metal concentrations of the tissues might be a result of their capacity to induce metal-binding proteins such as metallothionein (Canli and Atli, 2003; Uysal *et al.*, 2008).

4. Conclusion

In terms of food safety and based on the samples collected, the muscle tissue of all fish species might be considered suitable for human consumption, as the metal concentration levels observed were in the range of acceptable limits proposed by regulations of WHO and FAO especially the study of heavy metals.

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Author's Contributions

All authors discussed the results and contributed to from the start to final manuscript.

Conflict of Interest

The authors declare that they have no competing interests.

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