



**A COMPARATIVE STUDY ON THE
ACCUMULATION OF SOME HEAVY METALS
IN
BLUEFIN TUNA (*Euthynnus alletteratus*)
AND
SARDINELLA (*Sardinella aurita*)
IN THE COASTAL WATERS IN ZLITEN LIBYA**

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Abstract:

The toxicity of heavy metals and their accumulation in marine life make the most significant contaminants of the aquatic environment.

These metals can build up in fish tissues in varying concentrations, which can have a negative impact on human health if consumed in high quantities. Therefore, it is crucial to continuously evaluate the amounts of heavy metals in various fish species. Thus, the current study's aim was to examine the metal concentrations (Cu, Zn, Pb, Cd, and Hg) in the muscles, liver, gills, and gonad of round sardinella (*Sardinella aurita*) and bluefin tuna (*Euthynnus alletteratus*) that were collected in the Zliten Coast, Libya. The Atomic Absorption Spectrophotometer (AAS) was used to measure the concentrations of heavy metals. The findings revealed that the amounts of heavy metals in the two fish tissues varied significantly and were arranged as follows: Zn > Cu > Pb > Hg > Cd. Furthermore, both fish species showed accumulation level of Cu, Pb, Cd, and Hg was the highest in liver followed by gills, gonads, and lastly muscles, whereas Zn followed the pattern from the gonads to the liver, gills, and muscles, respectively. Thus, the study concluded that the levels of heavy metals in muscle tissue were within the FAO and WHO-recommended tolerable limits for human health.

Keywords: Heavy Metals, Accumulation, *Sardinella aurita*, *Euthynnus alletteratus*, Zliten Coast. Libya.

دراسة مقارنة لتحديد تراكم بعض المعادن الثقيلة في سمك التونة ذات الزعانف الزرقاء (*Euthynnus alletteratus*) وأسمك السردين السردينيلا (*Sardinella aurita*) في المياه الساحلية بمدينة زليتن ليبيا

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الملخص:

تعتبر المعادن الثقيلة من أهم ملوثات البيئة البحرية بسبب سميتها وقدراتها على التراكم في أجسام الكائنات الحية، هذه المعادن يمكنها ان تتراكم في أجسام الأسماك بكميات مختلفة وبالتالي يمكن ان يكون لها تأثير سلبي على صحة الانسان إذا استهلكت بكميات كبيرة، ولذلك فإنه من المهم تقدير مستويات المعادن الثقيلة في الأسماك باستمرار. لهذا السبب فإن هدف هذه الدراسة هو فحص تراكيز بعض المعادن الثقيلة والتي تشمل النحاس Cu والزنك Zn والرصاص Pb والكاديوم Cd والزرنيق Hg في عضلات وكبد وخياشيم والغدد التناسلية لأسماك السردين والتونا التي جمعت من الساحل البحري الليبي لمدينة زليتن. وقد أظهرت النتائج التي تم تحليلها باستخدام جهاز مطياف الامتصاص الذري ان تراكيز المعادن الثقيلة لنوعي الاسماك تحت الدراسة قد اختلفت اختلاف كبير وكانت مرتبة كما يلي ($Cd > Hg > Pb > Cu > Zn$) بالإضافة الى هذا فقد أظهرت النتائج ان المستوى التراكمي للمعادن الثقيلة الأتية Cu, Pb, Cd and Hg كان الأعلى في الكبد تليها الخياشيم تم الغدد التناسلية وان اقل هذه المستويات وجد في العضلات، اما بالنسبة الى Zn فإن النمط التراكمي هو الغدد التناسلية، الكبد، الخياشيم والعضلات على التوالي. وقد خلصت الدراسة الى ان تركيز المعادن الثقيلة في العضلات كانت ضمن الحدود المسموح بها من قبل منظمة الأغذية والزراعة ومنظمة الصحة العالمية.

الكلمات المفتاحية: المعادن الثقيلة، التراكم الحيوي، *Euthynnus alletteratus*، *Sardinella aurita*، ساحل زليتن، ليبيا.

1. INTRODUCTION

A semi-enclosed sea is the Mediterranean Sea, in regions surrounding the Mediterranean the environment is greatly impacted by human activity. The exploration, production and transportation of oil have significant environmental impacts. Also, the discharge of industrial and agricultural

waste as well as household sewage has an impact on the Mediterranean Sea. Because of all of this, the Mediterranean Sea has high concentrations of various contaminants, frequently close to the highest levels globally [1]. Beyond this, the exchange of Mediterranean water is very slow [2].

Because of their toxicity, persistence, bioaccumulation, and non-biodegradable qualities in the food chain, heavy metals are regarded as the most significant contaminants in the aquatic environment [3]. Due to their high protein, vitamin, and mineral content, fish are vital nutritional components. Consuming fish also provides omega-3 polyunsaturated fatty acids, which are known to lower the risk of heart disease, stroke, and preterm birth and are crucial for healthy growth [4]. In Libya, the most commercial consumed two fish species are *Euthynnus alletteratus* and *Sardinella aurita*.

Heavy metal contamination has grown and become a significant environmental and public health concern [5]. Bioaccumulation, biomagnification, and bio amplification in the food chain environment are characteristics of these metals [6]. Although essential heavy metals like copper and zinc are crucial for biological systems' metabolic processes, they can become potentially harmful when they reach certain threshold levels [7], [8]. On the other hand, non-essential metals like mercury, lead, and cadmium are poisonous, even at low concentrations, when consumed over an extended period [9], [10]. If the consumption of important metals is too high, they can also have harmful consequences [11], [12].

Fish can absorb heavy metals through their digestive tract, gills, or body surface. Although the surface of the body is thought to have a limited function in fish heavy metal absorption, gills are thought to be important locations for direct absorption from water [13], [11], [14]. Due to their high sensitivity to heavy metals fish organs like gills, liver and gonads are majorly studied for various kinds of fish species, heavy metals accumulate differently in these organs and are an essential bio-monitoring tool in assessing the level of toxicity in various fish species [15], [16] [17].

Heavy metal concentrations were measured in the livers, gills, muscles, skin, and bones of *Sardinella aurita* from the port of Tripoli, Libya [18], and in the gonads, liver, and muscle of *Euthynnus alletteratus* from the western part of Algeria [19].

Heavy metals tend to build up in the organs of marine life, particularly fish, and can later enter the human body and pose major health risks, therefore, it is crucial for human health to identify the levels of heavy metals in fish [17]. However, little is known about the amount of heavy metals in fish from Libyan water. Thus, the purpose of this study was to determine whether the muscles, livers, gills, and gonads of the more common fish species in Zliten City, *Euthynnus alletteratus* and *Sardinella aurita* were suitable for human consumption by analyzing the levels of several heavy metals (Cu, Zn, Pb, Cd, and Hg).

2. MATERIAL AND METHODS

2.1 Fish Gathering

In this investigation, fresh samples of two fish species—round sardinella (*Sardinella aurita*) and bluefin tuna (*Euthynnus alletteratus*) were used, that are mostly eaten by the locals in Zliten city (Libya).

2.2 Methods

On the day of capture, fish samples were purchased from local fishermen at Zliten Harbors, brought to the laboratory on ice, and then frozen at $-20\text{ }^{\circ}\text{C}$ until they were dissected.

For every fish species, ten samples were collected. The fish samples were weighed and measured to the nearest milligram and millimeter after being defrosted. Stainless steel dissection tools and medical gloves were used during the dissection process. The process for measuring out the concentration of heavy metal present in tissues has already been described [20]. Fish liver, gills, gonads, and epi-axial muscle (extracted from behind the dorsal fin) (about 1g) were put in small Erlenmeyer flasks and dried in an oven at $105\text{ }^{\circ}\text{C}$ for about 24 hours. The wet and dry masses of each sample were noted in order to calculate the moisture percentage for that sample. The materials were digested using concentrated nitric acid (65%) and perchloric acid (70%) in a 2:1 ratio. Digestion was performed at $200\text{--}250\text{ }^{\circ}\text{C}$ on a hotplate until the solution became transparent.

After allowing the samples to cool down to ambient temperature and filtering them, they were diluted using distilled water and kept in glass bottles that had been previously cleaned until the concentration of metals

could be ascertained. The amounts of Cu, Zn, Pb, Cd, and Hg were measured with an Atomic Absorption Spectrophotometer (NOV AA 400), $\mu\text{g metal/g wet weight}$ ($\mu\text{g/g w.w.}$) (ppm) was the unit of measurement for the amount of metal.

2.3 Statistical analysis

The data was statistically analysed using SPSS, and one way analysis of variance (ANOVA) was used to determine whether the amounts of heavy metals varied significantly. A P value of less than 0.05 was defined as statistical significance.

3. RESULTS

Low amounts of heavy metals are naturally present in marine life, but at high amounts, they can be harmful and interfere with aquatic ecosystems' biological processes. In a contaminated aquatic environment such as the Mediterranean Sea, fish that are exposed to high concentrations of metals have a tendency to absorb these metals from their immediate surroundings [21], [2]. Therefore, it may enter the human body and causes series effect [22]. The average and standard deviations of the amounts of Cu, Zn, Pb, Cd, and Hg in the muscles, gills, liver, and gonads of the fish species under investigation (*Sardinella aurita* and *Euthynnus alletteratus*) are displayed in Tables 1 and 2.

TABLE I. HEAVY METALS CONCENTRATIONS ($\mu\text{G/G W.W.}$) IN *Euthynnus alletteratus*

Organs Elements	Liver	Gills	Gonads	Muscls	Total
	Mean+SD	Mean+SD	Mean+SD	Mean+SD	Mean+SD
Cu	1.370±0.537	1.029±0.357	0.991±0.268	0.176±0.089	0.892±0.555
Zn	19.161±8.768	11.942±2.794	27.895±8.602	4.702±1.670	15.925±10.593
Pd	0.670±0.140	0.560±0.338	0.464±0.441	0.157±0.069	0.463±0.332
Cd	0.261±0.151	0.148±0.069	0.107±0.052	0.080±0.025	0.149±0.108
Hg	0.720±0.089	0.698±0.081	0.687±0.105	0.298±0.061	0.601±0.196

TABLE 2. HEAVY METALS CONCENTRATIONS ($\mu\text{G/G W.W.}$) IN *SARDINELLA AURITA*

Organs Elemnts	Liver	Gills	Gonaads	Muscls	Total
	Mean+SD	Mean+SD	Mean+SD	Mean+SD	Mean+SD
Cu	1.037 \pm 0.289	0.865 \pm 0.432	0.757 \pm 0.297	0.175 \pm 0.048	0.709 \pm 0.436
Zn	12.705 \pm 5.484	8.936 \pm 2.371	27.970 \pm 9.274	3.965 \pm 0.905	13.394 \pm 10.521
Pd	0.310 \pm 0.113	0.278 \pm 0.095	0.210 \pm 0.077	0.098 \pm 0.030	0.224 \pm 0.115
Cd	0.124 \pm 0.045	0.122 \pm 0.052	0.087 \pm 0.037	0.040 \pm 0.017	0.093 \pm 0.052
Hg	0.108 \pm 0.039	0.088 \pm 0.045	0.071 \pm 0.022	0.032 \pm 0.006	0.075 \pm 0.041

TABLE 3. INTERNATIONAL GUIDELINES FOR THE MAXIMUM AMOUNTS OF HEAVY METALS THAT CAN BE PRESENT IN FISH

Heavy Metals	<i>Euthynnus alletteratus</i>	<i>Sardinella aurita</i>	WHO (1993)	FAO (2009)
Cu	0.892 \pm 0.555	0.709 \pm 0.436	20.0 $\mu\text{g/g}$	30
Zn	15.925 \pm 10.593	13.394 \pm 10.521	100 $\mu\text{g/g}$	30
Pd	0.463 \pm 0.332	0.224 \pm 0.115	2.0 $\mu\text{g/g}$	0.5
Cd	0.149 \pm 0.108	0.093 \pm 0.052	0.5 $\mu\text{g/g}$	1.0
Hg	0.601 \pm 0.196	0.075 \pm 0.041	0.5 $\mu\text{g/g}$	0.5

4. DISCUSSION

The study's findings demonstrated the presence of the heavy metals under investigation in certain *Sardinella aurita* and *Euthynnus alletteratus* organs. Unlike Zn, which followed the sequence of gonads, liver, gills, and muscles, the bioaccumulation for Cu, Pb, Cd, and Hg by both fish species was generally in the following order liver, gills, gonads, and muscles these results are in contrast with other studies [23].

The concentration of Hg differed considerably among the fishes under investigation and among their organs (Table 1 and 2). *S. aurita* had the lowest concentration of Hg (0.075 ppm), whereas *E. alletteratus* had the greatest concentration (0.601 ppm).

According to the data presented, the liver had the highest concentrations of Cu, Pb, Cd, and Hg among all fishes examined, while the gonads had the highest concentration of Zn. Muscles showed the lowest metal concentrations, they seemed to be the least desirable location for metal

bioaccumulation (table 1 and 2). Research involving a variety of fish species has demonstrated that heavy metals mostly build up in highly metabolic organs like the liver, which stores metals in order to detoxify them by generating the protein metallothionein. [24], [25].

The current study found that fish muscles had the lowest concentration of heavy metals (table 1 and 2), this is well acknowledged because organs with low metabolic activity are less likely to accumulate heavy metals [26], [27], [28]. Lower numbers of binding proteins in muscle tissue could be the cause of the lower levels of heavy metals, including Cu, and Zn, in that tissue [29]. Following the liver, gills seemed to be the next most common organ for heavy metal accumulation (tables 1 and 2), the reason for this could be that fish gills have a particular role in absorbing metals from their surroundings, the gills have the thinnest epithelium of all the organs tested and are in direct contact with contaminated media (water) because of their respiratory function, which is designed for gaseous exchange with the environment [30]. Additionally, the gills may serve as a depot tissue, where metals are stored as their absorption greatly outweighs their removal [31].

Zinc concentrations were higher in gonads than in other fish organs (table 1 and 2), this is can be due to their involvement in the mechanisms of cellular growth and division, fertilization, and elimination of toxic metals. According to several studies gonads have been identified as a structure that is likely to have a high zinc concentration [32]. [23] stated that high levels of Zn were specifically detected in the gonads of the *Perca fluviatilis*, *Barbus barbus*, and *Silurus glanis*, and explained that the biological traits of these fish species, such as their preferred habitat or feeding habits, or environmental factors may be the cause of these elevated zinc levels in the gonads.

Many studies have shown that exposing fish species to a mixture of heavy metals, including Pb, Zn and Cu alters their gonadotropin and E2 profiles, which in turn affects their ability to reproduce [16], [33].

5. CONCLUSION

This study found that *E. alletteratus* has a good capability for accumulating mercury and might be used as a biological marker for mercury toxicity

research in open-sea environments. Despite being rarely eaten, fish livers could be useful bio-monitors of metals in the environment.

Given that the metal concentration levels found in the muscles of examined fish species were within the permitted range suggested by the World Health Organization (1990, 1993) (table 3), muscle tissue could be considered as safe for human consumption.

Considering certain biological and environmental elements of fish species, more research is required to identify the reasons behind the elevated zinc levels in the gonads

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