Journal of Radiation and Nuclear Applications
An International Journal

http://dx.doi.org/10.18576/jrna/090108

Estimation of Heavy Metals in the Bones of Selected Commercial Fish from the Eastern Libyan Coast

R. Hamad[1], *F. A. Ikraiam*[1*], *and H. Hasan*[2]

[1] Physics Department, Faculty of Science, Omar Al-Mukhtar University, EL-Beida, Libya.
[2] Chemistry Department, Faculty of Science, Omar Al-Mukhtar University, EL-Beida, Libya.

Received: 14 Sept. 2023, Revised: 12 Nov. 2023, Accepted: 27 Dec. 2023.
Published online: 4 Jan. 2024.

Abstract: Measurement of heavy metals concentration was carried out for fishbones of eight commonly-consumed fish inhabiting nine different locations in the Eastern Coastline of Libya, a distance of about 500 km. These fish are: Epinephelus Marginatus (S_1), Pagellus Bogaraveo (S_2), Pagellus Arcarna (S_3), Diplodus Vulgaris (S_4), Umbrina Cirrosa (S_5), Trachurus Mediterraneus (S_6), Balistes Carolinensis (S_7) and Seriola Dumerili (S_8). The chemical analysis was performed by an Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES). The obtained heavy metals were Cu, Pb, Cr, Zn, Co and Cd with concentrations not exceeding the limits of WHO guidelines for heavy metals and below the permissible safe limit value. Generally, the concentration of heavy metals in the studied samples were found to decrease in sequence of Zn > Pb > Cd > Cu > Cr > Co. Of these metals, the concentrations of Zn as an essential element were higher (except sample no. 4) than non-essential elements and the lowest were for Co, Cu and Cr. These results confirm the vital role of essential metals to fish species. Based on the results of the individual heavy metals values, with the exception of Pb, it is concluded that there was no health risk to humans due to consumption of these fish as far as heavy metal concentration is considered.

Keywords: Heavy Metals, Eastern Coast of Libya, Fishbones.

1 Introduction

Chemical safety and estimation of heavy elements in the environment are a major concern for the safety of public health. It is even more important if these elements are present in the food chain in concentrations higher than the permissible limits resulting in great risks to humans and living organisms as well as ecosystems due to their toxicity and bioaccumulation properties [1-2]. Trace metals such as copper (Cu), zinc (Zn) and manganese (Mg) are, however, essential metals since they perform important roles in natural ecosystems. On the other hand, non-essential metals, such as lead (Pb), cadmium (Cd), mercury (Hg), aluminum (Al) and arsenic (As), are generally toxic and their bioaccumulation in tissues may result in intoxication, infertility, cell and tissue damage or even cell death [3]. In the marine ecosystems, high-levels of heavy metals harm these ecosystems by decreasing species diversity [4]. Seas act as sinks for these metals which run through different aquatic chemical and biological cycles. For fish, the main aim of the present study, this represents the major input of these metals in fish both quantitatively and geographically where concentrations of heavy elements are significant for human health [5]. Contamination of marine life by heavy metals is a world-wide concern. Countries that have coasts on seas, such as Libya, have to deal with the coastal industries that discharge their wastes directly into the seas environments with little or no treatment. In Libya, main contributors to the seawaters and ground water pollution are the byproducts of various industries such as fertilizers, pesticides, chemicals, cement, construction and others. Subsequently, the sea ecosystems are influenced by chemical pollutant as a result of human activities. Solubility of heavy metals in water is believed to be one of the major environmental issues which, in turn, affects fish in seawaters [6-7]. Among all animal diversity of seawaters, fishes are the inhabitants which cannot escape from the damaging impacts of this pollution. Therefore, fish are usually chosen as bioindicator to check the seawater ecosystem health [8-12]. Major and heavy element rates should not exceed the permissible limits for edible fish. For this reason, estimating heavy metals in edible fish is important. According to the literature survey conducted for this paper, there are limited studies on radioactivity and heavy metals in fish and, nearly, no data found on the quality of edible fish supplies to the Libyan market [13]. Thus, to the best of the authors' knowledge, this is the first work to assess the levels of heavy metals in fishbones of

[*] Corresponding author e-mail: fawzi.ikraiam@omu.edu.ly

this area. This study is an attempt to fill this gap in the investigations and the estimations of heavy metals. The aim of the study is to measure the concentration of heavy metals in the eastern Libyan coast and to estimate the possible associated risk that may result in the consumption of these fish. The data obtained in this paper will provide a reference point and assist in establishing the background information for future studies on edible fish in the study area.

2 Materials and Methods

2.1 Study Area

The study area is the coast of eastern Libya (about 270 km along). It is situated between the city of Benghazi (latitude of 32˚12'92"N and longitude of 20˚09'16"E) in the west to the city of Altememi (latitude of 32˚33'35"N to longitude of 23˚07'69"E) on the Mediterranean Sea. The study area is mostly categorized by a rocky shoreline and a border coastline plain with intermingled sandy beaches and tiny inlets [13].

2.2 Collection and Preparation of Samples

Of the more than forty fish species documented in the coastline waters of the eastern part of Libya eight fish types were chosen in this study. The eight samples of the commonly consumed (edible) fishes (numbered S1 to S8) were collected from nine locations (numbered L1 to L9) in the study area as shown in Table 1.

Table 1. Location of sampling sites in the study area.

Site	S. No.	EL[a]	NL[b]
Benghazi (L1)	2, 3	20˚09'16"E	32˚12'92"N
Deryana (L2)	3	20˚32'86"E	32˚35'71"N
Toukra (L3)	4, 6, 8	20˚60'07"E	32˚53'38"N
Telmetha (L4)	1, 3, 5	20˚14'13"E	32˚42'01"N
Alhaneaa (L5)	2	21˚47'44"E	32˚82'73"N
Alhamaa (L6)	4	21˚61'39"E	32˚90'73"N
Souse (L7)	7	21˚96'64"E	32˚90'69"N
Khalig Albomba (L8)	1	20˚94'88"E	32˚70'91"N
Altememi (L9)	6	23˚07'69"E	32˚33'35"N
a EL=East Longitude, b NL=North Latitude			

Table 2 shows the eight sample fishes with their scientific, local and English names along with their collection locations. Samples were collected in different sizes and lengths to cover all fish ages.

Table 2. The eight studied fishes with their scientific and English names along with their site numbers.

S. No. (Site)	Scientific name	English name
1 (L4, L8)	Epinephelus Marginatus	Dusky grouper
2 (L2, L5)	Pagellus Bogaraveo	red sea bream
3 (L1, L2, L4)	Pagellus Arcarna	Axillary sea bream
4 (L3, L6)	Diplodus Vulgaris	two-banded sea bream
5 (L4)	Umbrina Cirrosa	Shi drum (Corb)
6 (L3, L9)	Trachurus Mediterraneus	Mediterranean horse mackerel
7 (L7)	Balistes Carolinensis	Trigger-fish
8 (L3)	Seriola Dumerili	great amberjack

The selected fish samples were transferred in an ice box to preserve these samples until transfer to the laboratory for analysis. The samples were washed with tap water and then distilled water. Samples then placed in the deep freezer until the digestion process. The collected fishes next were dried and washed several times with hot distilled water to remove the residue and soluble impurities. Fishes were left to dry in open air for enough time and then tissues were completely removed to end up with only fishbones. These samples were dried inside the oven at 60 ℃ until a weight stability was reached. Next, the fishbones were dried in an oven at 105 ^{o}C to be ashed. During ashing, low carbon nickel trays were used. The temperature for dry ashing varied but an upper recommended limit of 450 ℃ was used [14-15]. The dry bones were grinded in a plastic crucible until a powder form was attained. The samples were digested by weighing 2 grams of ground fish powder and placed in a conical glass flask, 10 mL of nitric acid and perchloric acid mixture at a ratio of 1: 1 (HNO3: HCLO4). Then these flasks were heated to a temperature of 160 ^{o}C until all volatile vapors are evaporated. The samples are placed in plastic containers for further analysis.

2.3 Heavy Metals Determination

Heavy-metal estimation in the environment and edible fish, in particular, is critical. The accurate measurement of concentrations of these metals is imperative to ensure that fishes are safe for human consumption. The heavy elements were measured using Perkin Elmer (2380) Atomic Absorption (AA) Spectrophotometer. Atomic spectroscopy is the technique for determining the elemental composition of an analyte by its electromagnetic or mass spectrum. AA is one of the three widely accepted analytical methods. The other two are atomic emission and mass spectrometry.

3 Results and Discussion

The eight fishbone samples were analyzed to calculate the concentrations (mg/L) of toxic elements and essential elements. The results showed the presence of these elements Cu, Pb, Cr, Zn, Co and Cd. Table 3 shows the concentration levels of the heavy metals detected in the samples. Figure 1 presents the concentrations of heavy metals in fishbone samples. Of these elements, Cd and Pb are toxic, while Cu, Zn and Co are essential elements. It is well known that Cu and Zn are required by a wide variety of enzymes and other cell components and having vital functions in all living organisms, but very high intakes can cause harmful health problems. On the other hand, Cd and Pb, have no biological role and hence they are harmful to living organisms even at considerably low concentrations. The calculated value of Cu varied from 0.16 to 0.25 with an average of 0.20 *mg/L*. Pb varied from 0.71 to 0.95 with an average of 0.80 *mg/L*. Cr varied from 0.13 to 0.31 with an average of 0.20 *mg/L*. Zn varied from 0 to 4.07 with an average of 3.12 *mg/L*. Co varied from 0.09 to 0.26 with an average of 0.16 *mg/L*. Finally, Cd varied from 0.06 to 0.46 with an average of 0.27 *mg/L*. The overall average concentrations of metals were found to accumulate in the following order. Sample no. 1, the order was Zn > Pb > Cr > Co > Cu > Cd. Sample no. 2, the order was Zn > Pb > Cd > Cr > Cu > Co. Sample no. 3, the order was Zn > Pb > Cd > Cu > Co > Cr. Sample no. 4, the order was Pb > Cd > Co > Cu > Cr, where Zn was not detected. Sample no. 5, the order was Zn > Pb > Cd > Cu > Cr > Co. Sample no. 6, the order was Zn > Pb > Cr > Cu > Co > Cd. Sample no. 7, the order was Zn > Pb > Cd > Cu > Cr > Co. While sample no. 8, the order was Zn > Pb > Cd > Cu > Cr > Co. Of these metals, the concentrations of Zn as an essential element were higher (except sample no. 4) than non-essential elements and the lowest were for Co, Cu and Cr. These results confirm the important role of essential metals to fish species [16-17]. Although it is not always the rule, these results were in conformity with the findings of other researchers, e.g. [18-19]. There was no single type of fish that was consistently high for all metals. The metabolic functions of the fish are also affected by the combined effect of nickel and chromium. Even though nickel was not detected in the studied samples, the results indicate that the heavy metal contamination definitely affects the aquatic life of fish. Regarding the daily intake and safety aspects, the studied fish may be safe for human consumption, with the exception of Pb where the concentration is higher than the recommended value found in literature, at least with regard to residual levels of cadmium, copper and zinc. Similar findings were reached by [20] for higher levels of Pb in fish in the western coast of Libya. However, it should be emphasized again that the present study is concerned with fishbones where heavy metals are expected to accumulate more than other parts of the fish.

Table 3. *Heavy metal concentrations in the fishbone samples (in mg/L).*

S. No.	***Cu***	***Pb***	***Cr***	***Zn***	***Co***	***Cd***
1	0.17	0.82	0.25	3.68	0.20	0.06
2	0.20	0.82	0.21	3.72	0.09	0.26
3	0.25	0.83	0.21	3.85	0.22	0.27
4	0.21	0.77	0.13	0	0.26	0.43
5	0.19	0.71	0.16	3.66	0.09	0.21
6	0.21	0.95	0.31	4.07	0.14	0.12
7	0.19	0.72	0.16	3.77	0.15	0.46
8	0.16	0.81	0.15	2.17	0.11	0.34
Ave.	0.20	0.80	0.20	3.12	0.16	0.27

The sources of heavy metals can be explained mainly by the geological structure of the region. Further research studies on the variations and the presence of heavy metals in the other parts of fish, like the liver, muscles, blood and so on, are required to determine the influence of heavy metal toxicity in fish in the study area. Based on the obtained results of this study and the importance of heavy metals in fish and their impacts on human health, continuous monitoring of heavy metals levels in fish is necessary.

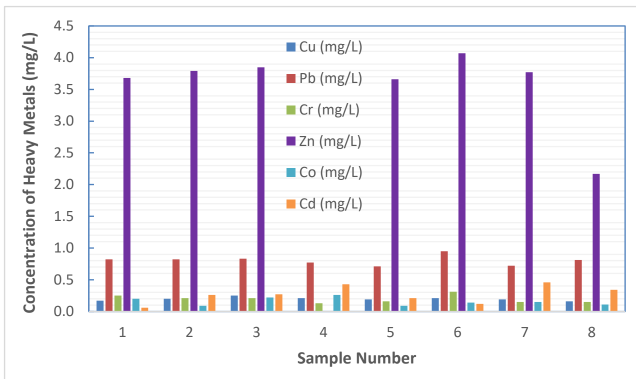

Fig.1. *Concentrations of heavy metals in fishbone samples.*

To the best of the author's knowledge, no Libyan safety standards are currently available regarding metal concentration in fish. While many literatures are available on heavy metal concentrations in fish, the majority of them were concerned either with different fish species, edible parts, or in the same fish species collected from different localities. No similar previous works were performed on fishbones and, hence, comparing our results with other studies is difficult and should be taken in precaution. Hence, assessment of heavy metal concentrations in fish must be performed on a regular basis to estimate human health risks from food intoxication and to purpose consumption suggestions and notifications [21].

4 Conclusions

In conclusion, this study was initiated to evaluate the level of heavy metals in selected fishbones from the eastern coast of Libya. Eight fish samples were collected from various sea shores of interest for commercial fishing industry from the study area. The study area extended from Benghazi city to Altememi city (a distance of about 500 km). The eight fish species are commonly consumed by the locals. These fish are: Epinephelus Marginatus, Pagellus Bogaraveo, Pagellus Arcarna, Diplodus Vulgaris, Umbrina Cirrosa, Trachurus Mediterraneus, Balistes Carolinensis and Seriola Dumerili. Heavy metals estimation was performed for bones of these samples. The concentration values (in mg/L) of these metals were: Cu varied from 0.16 for Seriola Dumerili to 0.25 for Pagellus Arcarna with an average of 0.20; Pb varied from 0.71 for Umbrina Cirrosa to 0.95 for Trachurus Mediterraneus with an average of 0.80; Zn from MDL for Diplodus Vulgaris to 4.07 for Trachurus Mediterraneus with an average of 3.12; Co from 0.09 for Pagellus Bogaraveo and Umbrina Cirrosa to 0.26 for Diplodus Vulgaris with an average of 0.16; Cd ranged from 0.06 for Epinephelus Marginatus to 0.46 for Balistes Carolinensis with an average of 0.27; Cr ranged from 0.13 for Diplodus Vulgaris to 0.31 for Trachurus. The overall average concentrations of metals, in general, were found to accumulate in the following order: Zn > Pb > Cd > Cu > Cr > Co. Of these metals, the concentrations of Zn as an essential element were higher (except sample no. 4) than non-essential elements and the lowest were for Co, Cu and Cr. The obtained results for the heavy metal levels were lower than the worldwide allowable limits with the exception of Pb. Hence, in general, the values of the obtained heavy levels in the selected fish samples do not pose radiological risks at the time of this study with the exception of Pb where this increase in Pb may be of concern to consumers of these types of fish. The results of this study could serve as an important radio-metric baseline data, upon which future epidemiological studies and environmental monitoring initiatives could be based and a reference data in future in the study area. The data obtained represent an additional contribution in the study area, which are crucially lacking, where none was previously available. A continuous monitoring of heavy metals in edible fish is essential to be within allowable worldwide limits. Precaution measures also need to be taken in order to prevent future heavy metal pollution.

Funding: This research received no funding.

Conflicts of Interest: The authors declare no conflict of interest.

References

[1] D. Deforest, K. Brix and W. Adams, Assessing Metal Bioaccumulation in Aquatic Environments: The Inverse Relationship between Bioaccumulation Factors, Trophic Transfer Factors and Exposure Concentration, Aquatic Toxicology, 84, 236-246, 2007.

[2] F. Fu and Q. Wang, Removal of Heavy Metal Ions from Wastewaters: A Review, Journal of Environmental Management, 92, 407-418, 2011.

[3] P. Govind and S. Madhuri, Heavy Metals Causing Toxicity in Animals and Fishes, Research Journal of Animal, Veterinary and Fishery Sciences, 2(2), 17-23, 2014.

[4] T. Hosono, C. Su, R. Delinom, Y. Umezawa, T. Toyota, S. Kaneko and M. Taniguchi, Decline in Heavy Metal Contamination in Marine Sediments in Jakarta Bay, Indonesia Due to Increasing Environmental Regulations Estuarine, Coastal and Shelf Science, 92, 297-306, 2011.

[5] K. Taslima, Md Al-Emran, M. Shadiqur Rahman, J. Hasan, Z. Ferdous, Md Fazle Rohani and Md Shahjahan, Impacts of heavy metals on early development, growth and reproduction of fish–A review, Toxicology Reports, 9, 858-868, 2022. DOI:10.1016/j.toxrep.2022.04.013

[6] A. Waseem, J. Arshad, F. Iqbal, A. Sajjad, Z. Mehmood and G. Murtaza, Pollution Status of Pakistan: A Retrospective Review on Heavy Metal Contamination of Water, Soil and Vegetables, BioMed. Research International, 1-29, 2014.

[7] C. Hong and C. Haux, Binding and Detoxification of Heavy Metals in Lower Vertebrates with Reference to Metallothionein, Comparative Biochemistry and Physiology, Part C, 100-137, 2008.

[8] I. Inayat, A. Batool, M. F. Rehman, N. Humanaveed, H. Jabeen and H. Bibi, Seasonal variation study for the accumulation of Cu, Pb and Mn in Kidneys, liver and Muscles of different edible fish from River Jhelum, Punjab, Pakistan, Scholars Bulletin, 3 (1), 23-27, 2017.

[9] E. R. Atta and K. H. Zakaria, Evaluation of Some Radioactive Materials and Heavy Metals in Marine Environment of Alexandria Coastline, Egypt, Journal of Environmental Protection, 5, 1618-1629, 2014.

[10] J. O. Nriagu and J. M. Pacyna, Quantitative assessment of worldwide contamination of air, water and soils by trace metals, Nature, 333, 134-139, 1988.

[11] J. Burger, K. Cooper and M. Gochfeld, Exposure assessment for heavy metal ingestion from a sport fish in Puerto Rico: estimating risk for local fishermen, J. Toxicol. Environ. Health., 36, 355-365, 1992.

[12] A.Farkas and J. Salánki and A. Specziár, Relation between growth and the heavy metal concentration in organs of bream Abramis brama L. populating Lake Balaton. Arc. Environ. Contam. Toxicol., 43, 236-243, 2002. DOI:10.1007/S00244-002-1123-5

[13] R. Hamad, F. A. Ikraiam and H. Hasan, Determination of Specific Natural Radionuclides in the Bones of Some Local Fish Commonly Consumed from the Eastern Libyan Coast, Journal of Radiation and Nuclear Applications, 3, 283-289, 2023.

http://www.naturalspublishing.com/Journals.asp
[14] IAEA, Measurement of Radionuclides in Food and the Environment: A Guidebook, IAEA Technical Report Series no. 295, VIENNA (STI/DOC/10/295), 1989.
[15] UNSCEAR. Effects of Radiation on the Environment: Sources and effects of ionizing radiation. United Nations Scientific Committee on the Effects of Atomic Radiation (UNSCEAR), New York, Report to the General Assembly, with Scientific Annex, United Nations, New York. 2000.
[16] T. Yahaya, Y. Abdulganiyu, A. Abdulazeez, O. C. Dikko, D. M. Bashar, U. F. Mohammed, Z. A. Mohammed, U. U. Liman, Characterization and Health Risk Evaluation of Water and Fish Samples obtained from Ogun River in Lagos, Nigeria, J. Mater. Environ. Sci., 13 (4), 424-534, 2022.
[17] P. R. Fresquez, D. H. Kraig, M. A. Mullen and L. Naranjo Jr., Radionuclides and Trace Elements in Fish Collected Upstream and Downstream of Los Alamos National Laboratory and the Doses to Humans from the Consumption of Muscle and Bone. Journal of Environmental Science and Health, Part B, 34 (5), 885-899, 1999. DOI:10.1080/03601239909373233
[18] M. Bahnasawy, A. Khidr and N. Dheina, Seasonal variations of heavy metals concentrations in Mullet, Mugil cephalus and Liza ramada (Mugilidae) from Lake Manzala, Egypt, J. Appl. Sci. Res., 5, 845–852, 2009.
[19] Y. Chen and M. Chen, M., Heavy metal concentrations in nine species of fishes caught in coastal waters off Ann-Ping, S.W Taiwan, J. Food Drug Anal., 9, 107-114, 2001.
[20] H. Hadeed. Effect of heavy metals on the physiological parameters of some fish species in cost of Misurata., M. Sc thesis, (in Arabic), Libyan Academy, Libya, 2017.
[21] S. H. Q. Hamidalddin and J. H. AlZahrani, An Assessment of Some Toxic, Essential Elements and Natural Radioactivity, in Most Common Fish Consumed in Jeddah-Saudi Arabia, Journal of Food and Nutrition Sciences, 7, 301-311, 2016. DOI:10.4236/fns.2016.74032