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Bioaccumulation Study of Some Heavy Elements in Three Fish Species Collected from Zlitan Beaches, Libya

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دراسة التراكم الحيوي لبعض العناصر الثقيلة لثلاث أنواع من الأسماك المجمعة من شواطئ مدينة زليتن، ليبيا

الملخص:

تناولت هذه الدراسة قياس معدل التراكم الحيوي لبعض العناصر الثقيلة (الرصاص Pb، الكادميوم Cd، الزنك Zn) في عينات ثلاث أنواع من أسماك بحر الابيض المتوسط في دولة ليبيا في مدينة زليتن (سمك البوري، سمك الكوالي، سمك االسردين) من المنطقة الممتدة من شاطئ عين كعام إلى منطقة شاطئ الدافنية من ثلاث مواقع وهي (موقع عين كعام، موقع مرسى زليتن، موقع شاطئ الدافنية) والتي تم جمعها في يونيو2023 م، جمعت من كل نوع 20 سمكة، ونقلت إلى المعمل حيث تم قياس أطوالها وقياس أوزانها وأجراء عليها الهضم الرطب، ثم نقلت عينات ماء البحر وعينات كبد الأسماك المهضومة إلى مركز المتقدم للتحليل الكيميائي في تاجوراء. وقد أظهرت النتائج ارتفاع تركيز المعادن في أغلب العينات عن الحدود المسموح بها حسب منظمتي (WHO/FAO) World Health Organization) و Food and Agriculture Organization)، ووضعت النتائج في جداول خاصة بها، فكان تركيز معدن الكادميوم والرصاص في أكباد الأسماك المدروسة أعلى من الحدود المسموح به للأنواع الثلاثة من الأسماك ومواقع المدروسة الثلاثة وهو5 (µg/g)، وهو(6 µg/g)، تجاوز تركيز المعدن الزنك في أكباد الأسماك المدروسة في حدود المسموح به وهو1 (µg/g) للأنواع الثلاثة من الأسماك ولمواقع المدروسة الثلاثة بمتوسط 3.18(µg/L) وكان البوري أعلاها.

وقيست الوظائف الفسيولوجية لأنزيمات الكبد للأسماك المدروسة، يوصى بتكثيف الأبحاث العلمية على الأحياء المائية لغرض معرفة مدى تلوثها بمختلف العناصر الثقيلة وذلك لمنع وصولها إلى السلسة الغذائية.

ثم حسب التراكم الحيوي (BCF) (ميكروجرام/لتر) للمعادن الثلاثة بأكباد الأسماك بحسب موقع الصيد ونوع الأسماك، وسجلت في جداول خاصة بها، وحسبت المتوسطات الحسابية والانحرافات المعيارية ووضعت بجداول، ونوصي حماية البحار والمحيطات من مخاطر التلوث على اختلاف أشكاله وصوره، عدم أكل الأسماك خارج المنزل إلا في المطاعم النظيفة لمنع حدوث التسمم.

الكلمات الدالة: *التراكم الحيوي، سمكة البوري، سمكة السردينة، العناصر الثقيلة الرصاص، الزنك، الكادميوم، أنزيمات الكبد.*

Abstract:

This study focused on measuring the bioaccumulation rate of certain heavy elements (lead Pb, cadmium Cd, zinc Zn) in the livers of three Mediterranean Sea fish species collected from Zliten beaches in Libya: bouri fish, quala fish, and sardine fish. The samples were obtained from three different locations: Ain Kaam Beach, Mersa Zliten, and Dafnia Beach, in June 2023. Each type of fish had 20 samples, which were preserved in ice to prevent spoilage. The samples were then transported to the Advanced Center for Chemical Analysis in Tajura.

The results showed elevated metal concentrations in most of the studied samples, exceeding permissible limits according to the World Health Organization (WHO) and the Food and Agriculture Organization (FAO):
•Cadmium and Lead, concentration in fish livers exceeded the permissible limit for all three fish species and locations (5 µg/g) and (6 µg/g).
•Zinc concentration in fish livers did not exceed the permissible limit (1 µg/g) for all three fish species and locations, with an average of 3.18 µg/L. Bouri fish had the highest zinc concentration .we assessed the effect of heavy metal concentrations (lead, cadmium, and zinc) in fish livers on the levels of liver enzymes (AST, LDH, ALT, ALP). Lead concentration had a significant positive effect on all four enzymes to varying degrees. Cadmium concentration had a positive effect on three liver enzymes (ALT, ALP, AST), while zinc concentration did not significantly affect any of the enzymes.
Thus, sardine fish exhibited the lowest elevation in liver enzymes among the three studied fish species.
Finally, we presented the results of the bioconcentration factor (BCF) calculations for the three metals—cadmium, lead, and zinc—in fish livers based on fishing location and fish type
Keywords: *Bioaccumulation, Bouri fish, Sardine fish, Heavy elements, Lead, Zinc, Cadmium, Liver enzymes.*

Introduction:

Fish play a crucial role in the human diet in many parts of the world. They contribute to solving global food challenges by providing proteins, minerals, and vitamins. Consequently, concerns about the impact of human-induced pollution on ecosystems are growing. Heavy metals are continuously released into aquatic and terrestrial ecosystems from human-made pollution sources, posing a serious threat due to their toxicity, bioaccumulation, and biomagnification in the food chain (Sinicropi et al., 2010). In recent years, there has been increased interest in heavy metal concentrations in fish and other foods to assess their potential health risks to humans (Carocci et al., 2014).

The Mediterranean Sea is one of the world's most important seas due to its geographical location. It lies between three continents (Africa, Asia, and Europe) and is bordered by 18 countries. Libya, among these countries, has a coastline approximately 1800 km long, which has led to a diverse fish population (Ahmed et al., 2009). The availability of fish species such as bouri, quala, and sardine is high, making them popular choices for consumption among the population. Their nutritional characteristics and affordability contribute to their demand in Libyan fish markets (Al-Sarraj et al., 2013).

Bioaccumulation of heavy metals varies across different species, ages, genera, and organs of living organisms. Fish meat is highly nutritious, containing essential amino acids, minerals, and vitamins necessary for human nutrition. Additionally, fish have low saturated fat content (Dabbagh et al., 2011; Belaid et al., 2019). Heavy metals, in general, are characterized by their physical properties, including being transition metals or semimetals with a density greater than 5 g/cm³. They are commonly referred to as toxic metals (Al-Jatlawi et al., 2017).

Water pollution by heavy metals results from human activities, and this pollution poses a serious risk to living organisms (Casado et al., 2008; Al-Jatlawi et al., 2017). Environmental pollution at the global level has led to the contamination of fish with harmful substances (such as pesticides, sewage, industrial, and agricultural runoff). The presence of heavy metals in fish indicates the extent of water pollution by these metals in a specific location (Al-Adl et al., 1995). The darkening of the peritoneal membrane in fish is a strong indicator of heavy metal pollution, and larger fish are more dangerous because they consume smaller fish containing heavy metals, leading to higher toxin accumulation (Salman et al., 2007).

Fish are used as bioindicators in environmental monitoring programs to assess water pollution levels. They serve as indicators of heavy metal contamination in the environment they inhabit. Heavy metals can enter aquatic food chains, especially fish, either directly through food or indirectly through trophic interactions. The impact of heavy metals can be transferred from one organism to another through the food chain, ultimately affecting human consumers at the top of the food pyramid. Fish have a higher capacity to concentrate pollutants than water and sediments due to their feeding habits on small organisms and organic matter present in the aquatic environment (Carocci et al., 2014).

Materials and Methods:

The follo wing equipment was used : Balance , Centrifuge , Electric oven , Atomic Absorption Spectroscopy (AAS) instrument , Enzyme analysis device , Electric blender .

The chemicals used were as follows:

Concentrated nitric acid (HNO_3, 65%), Concentrated perchloric acid ($HClO_4$, 65%), Concentrated sulfuric acid (H_2SO_4, 65%), Sodium chloride (NaCl, 8 mL), Potassium chloride (KCl, 2 mL).

Sampling Area:

Samples Potassium chloride (KCl, 2 mL were collected from three different locations along the Libyan coastline, stretching approximately 177 kilometers from Ain Kaam Beach to Dafnia Beach. The three sampling sites were: Dafnia Beach , Mersa Zliten, Ain Kaam

Statistical Analysis:

The data of the studied samples were processed and analyzed using the statistical program SPSS 20 for data analysis, and to find the correlation between the type of studied fish and the type of heavy metal using Spearman Rank Correlation test. The Pearson correlation test was used to study the relationship between the concentrations of heavy metals in seawater and the enzyme concentrations in the liver tissue of the studied fish. For drawing charts, Microsoft Excel 2010 was used. The significance of the linear regression was tested when studying the effect of an independent variable on a dependent one, and differences between means were tested at a significance level of $\alpha=0.05$. The bioconcentration factor is calculated according to the following equation:

Bioconcentration Factor (BCF) = Concentration of the metal in the fish (EC)/ Concentration of the metal in seawater (ECW) (Amin et al., 2007).

Measured in micrograms per liter.

Results and Discussion :

The study showed that the highest values for lead concentration in the Mediterranean Sea, according to the study site, were recorded at Marsa Zliten. This may be due to its high concentrations in the aquatic environment at this site. The reason might also be the presence of Zliten General Hospital and several clinics near this port, which dispose of medical waste untreated into the sea, thus increasing the metal content in the seawater at this studied site. Consequently, the studied fish that feed in these waters have increased metal concentrations in their livers, as indicated in the study by Akbar et al., 2012. Additionally, waste from ships and boats, waste from ship oil change workshops, car wash parking lots that are dumped into sewage waters, household waste, and industrial waste contribute to this pollution (Abbas et al., 2007). It was also observed that the highest concentrations of zinc were at Dafniya Beach, which might be due to its location in residential areas where pollution results from household waste disposal. Moreover, it is located near a sewage outlet (Ortiz et al., 2003).

The results showed that the average concentration of the studied heavy metals varied according to the type of metal, fish species, and the location where these fish live. This is consistent with findings by Ahmed et al., 2010. This variation in heavy metal concentration in the livers of different fish species was statistically significant, while the variation in metal concentration in the livers of the same fish species living at the same site was not statistically significant, aligning with findings by Al-Sarraj et al., 2014. Our study revealed a significant relationship between heavy metal concentration and liver enzymes in the studied fish, which agrees with Abker's study (2004).

Correlation and Regression Analysis:

The study demonstrated a direct relationship between the concentration of three metals—lead, cadmium, and zinc—in seawater at three studied sites: Ain Kaam, Marsa Zliten, and Dafniya Beach—and liver enzyme concentrations in fish livers of three species. This is consistent with Abedi et al.'s study (2013).

Data Analysis and Presentation of Results:

1-2-1: Presentation of results for heavy metal concentration analysis—cadmium, lead, and zinc—in seawater according to the studied site and fish species: For lead concentrations measured in (µg/L),

Marsa Zliten > Ain Kaam > Dafniya Beach.

For cadmium concentrations measured in (µg/L),

Ain Kaam = Marsa Zliten; Marsa Zliten > Dafniya Beach; Ain Kaam > Dafniya Beach.

For zinc concentrations measured in (µg/L),

Ain Kaam = Marsa Zliten; Marsa Zliten > Dafniya Beach; Ain Kaam > Dafniya Beach.

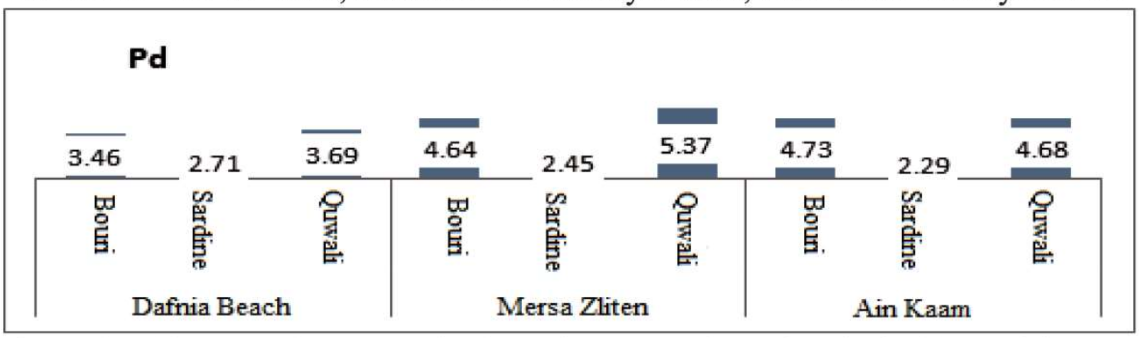

Figure (1): Illustrates the average lead metal concentration (g/µg) in the livers of the studied fish, according to the study site and fish type.

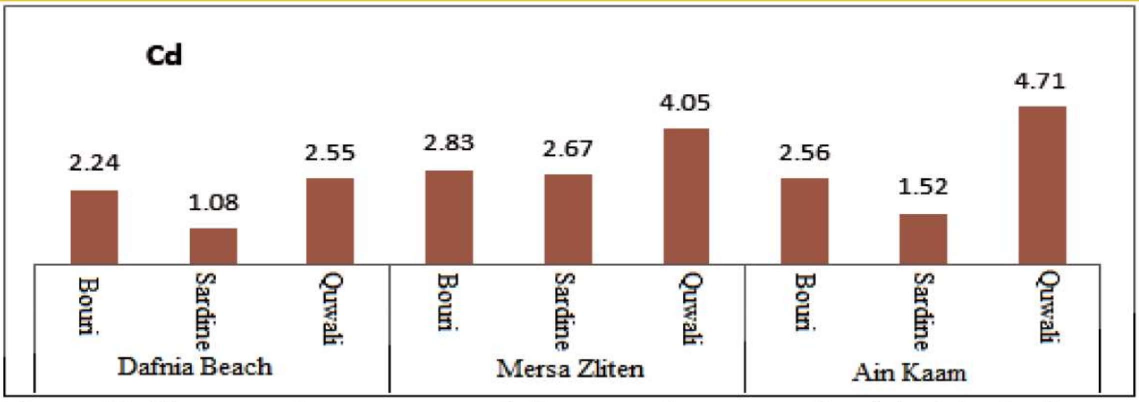

Figure (2): Illustrates the average cadmium, metal concentration (g/µg) in the livers of the studied fish, according to the study site and fish type.

Thirdly: A study of liver enzyme concentrations (ALP-AST-LDH-AST) in fish samples that underwent statistical analysis. These samples were collected in June 2023 from each of the following sites: Ain Kaam, Mersa Zliten, and Dafnia Beach, based on the studied location and the type of fish examined there.

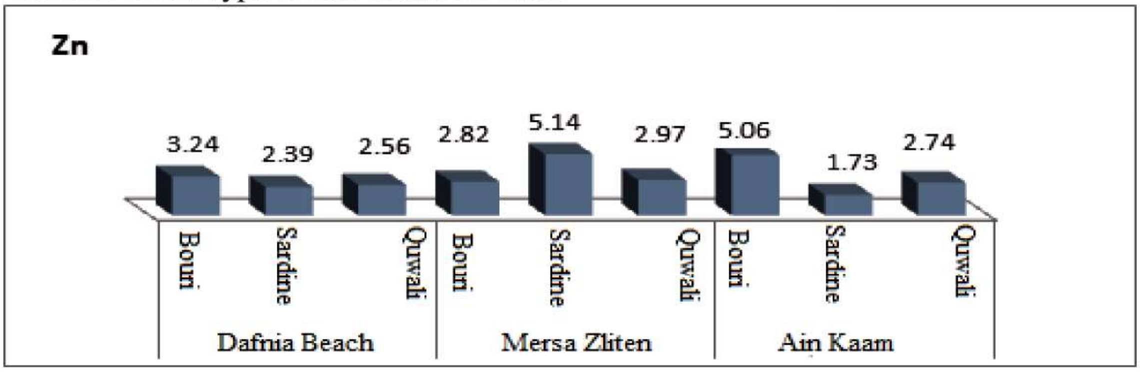

Figure (3): Illustrates the average zinc metal concentration (g/µg) in the livers of the studied fish, according to the study site and fish type.

Thirdly:

A study of liver enzyme concentrations (ALP-AST-LDH-AST) in fish Figure 19 illustrates the average concentration of the enzyme ALP in the livers of the studied fish, categorized by fish type and study location.on the studied location and the type of fish examined there.

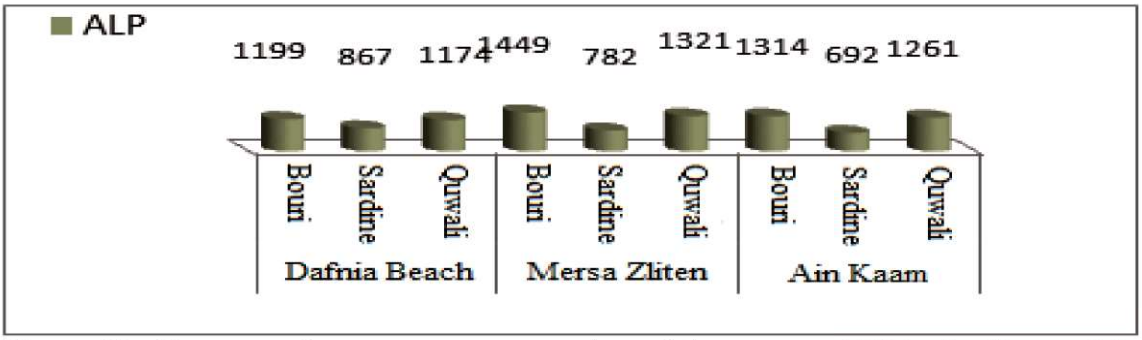

Figure (4): Illustrates the average concentration of the enzyme ALP in the livers of the studied fish, categorized by fish type and study location.

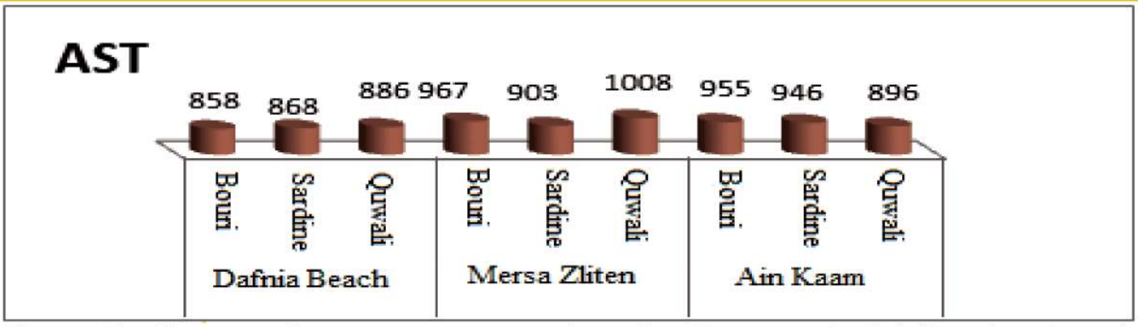

Figure (5): Illustrates the average concentration of AST enzyme in fish liver based on the studied fish species and location.

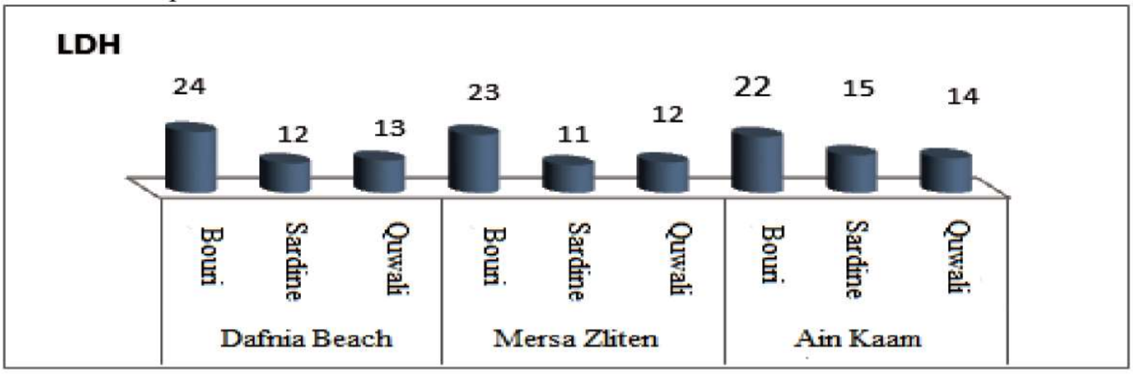

Figure (6): Illustrates the average concentration of LDH enzyme in fish liver based on the studied fish species and location.

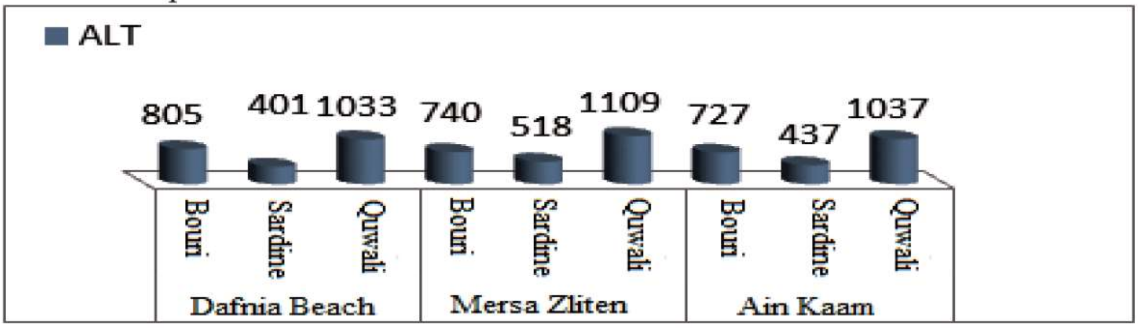

Figure (7): Illustrates the average concentration of the enzyme ALP in fish livers according to the type of studied fish and the studied location.

The results of the correlation and regression:

analysis indicate that sig > 0.05 for all relationships. This implies that there is no significant correlation or significant effect between the concentration of heavy metals in seawater and the concentration of heavy metals in the livers of the fish.

Table (1): Illustrates the correlation between the average concentration of heavy metals in seawater and the concentration of heavy metals in the livers of the fish studied.

zinc		cadmium		lead		
Regression **sig**	**R**	**sig** regression	**R**	Regression **Sig**	**R**	
0.642	0.035	0.89	0.01	0.713	0.028	Ain Kaam
0.726	0.026	0.989	0.001	0.813	0.018	Mersa Zliten
0.765	0.022	0.894	0.01	0.511	0.049	Dafnia Beach

Table (2): Illustrates the effect of lead concentration on the liver of the studied fish and its impact on liver enzymes.

The effect of lead metal concentration in studied fish			
Regression Sig.	Adjusted R Square	R	Enzyme concentration
0.000	0.230	0.484	AST
0.000	0.066	0.267	LDH
0.000	0.516	0.720	ALT
0.000	0.417	0.648	ALP

Table (3): Illustrates the effect of lead concentration on the liver of the studied fish and its impact on liver enzymes.

Effect of lead concentration on the liver of the studied fish and its impact on liver enzymes.			
Regression Sig.	Adjusted R Square	R	Enzyme concentration
0.540	0.003	0.046	AST
0.125	0.008	0.115	LDH
0.498	0.003	0.051	ALT
0.588	0.004	0.041	ALP

Table (4): Illustrates the effect of cadmium metal concentration in the livers of the studied fish on the concentration of liver enzymes.

Effect of cadmium metal concentration in the livers of the studied fish on the concentration of liver enzymes.			
Regression Sig.	Adjusted R Square	R	Enzyme concentration
0.000	0.095	0.316	AST
0.184	0.004	0.100	LDH
0.000	0.564	0.753	ALT
0.000	0.164	0.410	ALP

Bioaccumulation of lead:

The results indicate that the rate of bioaccumulation of heavy metals (cadmium, lead, and zinc) in fish livers within the same aquatic environment varies. Notably, the highest bioaccumulation values were observed in the livers of mullet fish at the Mersa Zliten site, surpassing the bioaccumulation of heavy metals in both sardine and mackerel fish. This increase can be attributed to the mullet fish's diet, which includes smaller fish that already contain heavy metals in their livers. Additionally, the mullet fish reside in waters contaminated with heavy metals, leading to a greater accumulation of these metals in their livers compared to other fish species. These findings align with previous research by (Carocci et al. 2014).

The bioaccumulation of heavy metals in marine organisms depends on several factors, including:

The concentration of the metal in the aquatic environment and its chemical form.

The timing of exposure relative to the seasons.

Environmental factors that significantly impact the absorption and accumulation of metals in marine organisms. For instance, temperature contributes to increased bioaccumulation due to higher metabolic rates, including enhanced absorption and accumulation, especially in more active organs such as the kidneys and liver (Fattaloui et al., 2017).

Table (5): Which represents the average bioaccumulation of lead (Pb) according to the studied site and fish type.

Bioaccumulation of lead	Fish Type	Location
1.2	Quwali	Ain Kaam
0.6	Sardine	
1.2	Bouri	
1.0	Total Kaam	
1.1	Quwali	Mersa Zliten
0.5	Sardine	
1.0	Bouri	
0.9	Total Zliten	
1.1	Quwali	Dafnia Beach
0.8	Sardine	
1.01	Bouri	
0.96	Total Dafnia	
0.9	Overall Mean	

Table (6): Which represents the average bioaccumulation of cadmium (Cd) according to the studied site and fish type.

Bioaccumulation of Cd	Fish Type	Location
5.6	Quwali	Ain Kaa
1.8	Sardine	
3.0	Bouri	
3.5	Total Kaam	
5.1	Quwali	Mersa Zliten
3.4	Sardine	
3.6	Bouri	
4.0	Total Zliten	
6.0	Quwali	Dafnia Beach
2.5	Sardine	
5.2	Bouri	
4.6	Total Dafnia	
4.0	Overall Mean	

Table (7): Which represents the average bioaccumulation of zinc (Zn) in fish bodies according to the studied site and fish type.

Bioaccumulation of zinc	Fish Type	Location
1.0	Quwali	Ain Kaa
0.6	Sardine	
1.9	Bouri	
1.2	Total Kaam	
1.0	Quwali	Mersa Zliten
1.8	Sardine	
1.0	Bouri	
1.3	Total Zliten	
1.0	Quwali	Dafnia Beach
0.9	Sardine	
1.3	Bouri	
1.1	Total Dafnia	
1.2	Overall Mean	

Summary:
Through statistical analysis of data from 20 fish of each species - mullet, sardine, and seabream - caught in June 2023 from Ain Kaam, Marsa Zliten, and Dafniya Beach, we studied liver enzyme concentrations (AST, DH, ALT, ALP) and heavy metal accumulation (lead, cadmium, zinc) in their livers. The lead concentration in the fish livers was higher than the permissible limit of 6 µg/L for all three species and locations. Zinc concentration exceeded the permissible limit of 1 µg/L with an average of 3.18 µg/L, with seabream having the highest levels.

Physiological Function Assessment of Liver Enzymes :

ALP: All concentrations were above the permissible limit of 100 U/L, with seabream showing the highest levels.

AST: All concentrations exceeded the permissible limit of 100 U/L, with mullet and seabream equally highest.

LDH: All levels were above the permissible limit of 1 U/L, with seabream being the highest.

ALT: All concentrations were above the permissible limit of 30 U/L, with sardines showing the lowest enzyme elevation among the three species.

Impact of Mediterranean Sea Heavy Metal Pollution on Studied Fish Liver Enzymes: Lead concentration significantly affected all four enzymes to varying degrees:

ALT: Above-average direct significant effect (R=0.72).

ALP: Above-average direct significant effect (R=0.648).

AST: Average direct significant effect (R=0.484).

LDH: Weak direct significant effect (R=0.267).

Cadmium concentration affected three liver enzymes significantly but not the fourth:

ALT: Above-average direct significant effect (R=0.753).

ALP: Above-average direct significant effect (R=0.410).

AST: Average direct significant effect (R=0.316).

Zinc concentration did not significantly affect any enzymes. The three enzymes ALT, ALP, and AST were affected by lead and cadmium concentrations in the same sequence but not by zinc concentration. The cause of elevated liver enzymes in studied fish remains unclear despite significant direct correlations found with heavy metal concentrations that were not elevated. The bioaccumulation of heavy metals is considered high when compared to the highest natural bioaccumulation values.

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