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Investigation of Toxic Metals Pollution in Water, Sediment and Fish at Al-Hodeida city, Red Sea Coast of Yemen

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ABSTRACT

The discharge of industrial waste and sewage is unequivocally the primary cause of toxic metal pollution in the Red Sea. This study centers on the detrimental impact of these human activities on the coastal ecosystem. We did an investigation because there was no available data on the levels of hazardous metals in the Red Sea Coast of Yemen. This study analyzes the average levels of toxic metals - Pb, Cd, Hg, and As - in water, sediments, and various fish organs including muscle, liver, and gill. Acquired from Al-Hodeidah city, situated on the Red Sea Coast of Yemen. Examples of water and debris have been gathered at nine different locations. Four fish species (Lethrinus mahsena, Epinephelus areolatus, Thunnus tonggol, and Sphyraena jello) were acquired from local commercial fisherman in Al-Hodeidah city between 2022 and 2023. Pb, Cd, Hg, and As levels were tested in water at 0.053-0.105, 0.006-0.008, 0.006-0.008, and 0.007-0.009 mg/l respectively. In sediment, the levels were 75.883-77.059, 2.380-2.495, 0.011-0.028, and 0.091-0.109 µg/g dry weight for Pb, Cd, Hg, and As respectively. Levels of toxic metals in fish tissue (µg/g dry weight) vary as follows: Pb 0.031-0.357, Cd 0.018-0.146, Hg 0.019-0.082, and As 0.044-0.121 µg/g dry weight in muscle; Pb 0.058-1.466, Cd 0.057-0.700, Hg 0.009-0.044, and As 0.011-0.074 dry weight in gills; and Pb 0.049-0.999, Cd 0.047-0.705, Hg 0.051-0.186, and As 0.065-0.198 µg/g dry weight in liver cells. Comparing data from local and international studies along with global and local contamination standards, it is clear that pollution concentrations in Yemen are currently lower than the established limits

INTRODUCTION

Aquatic system contamination is a significant global concern.Various sources contaminate aquatic systems with heavy metals .(Abdel-Baki et al.2011) . These consist of animal matter, wet and dry depositions of air particulate matter, and human activities. Parameters such as pH and temperature influence heavy metal content, the bioavailability and toxicity in aquatic systems (Belin, S.; Sany, T. and Salleh, A 2018). Municipal sewage discharge originates from urban or densely populated residential regions, whereas industrial wastewater comes from a range of manufacturers (Wu, Y. and Chen, J 2018). Heavy metals will partition between the aqueous phase and bed sediments in aquatic systems.Sediment plays a crucial role in the water environment by accumulating contaminants from the water and acting as a secondary source of pollution that can affect water quality .(Varol, M.; and Şen, B. 2017). Thus, sediment quality serves as a reliable indicator of water column pollution, as it has a tendency to accumulate heavy metals (Wang, C et al.2021). Metallic substances are found in soils in four portions: exchangeable bound, iron-manganese oxide, organic matter, and residual species (Wang, C et al.2021). Due to their biological significance and the long-lasting nature of contaminants in the aquatic environment, sediments are better suited for monitoring in environmental assessments to comprehend their potential harmful effects. Fishes are the top consumers in the aquatic ecosystem. Fish can accumulate these metals in higher amounts than water and sediments due to their consumption of organic matter in aquatic ecosystems. Fish are effective indicators of heavy metal contamination in aquatic environments due to their presence at various trophic levels. Food can also serve as a significant source of heavy metal buildup in fish.Metals in aquatic ecosystems are passed on to fish through the food chain, potentially impacting the health of humans who eat these species.Industrial and home waste containing heavy metals can build in aquatic food chains, potentially causing acute and chronic harm to fish communities.(Schulz, U. H. and Martins-Junior 2001).

Lead in water builds up in fish bodies and is later consumed by humans who eat these fish.The human body sustains damage to the neurological system due to the presence of Pb. (Mason, L. H. (2014). Caution is advised due to the quantities of cadmium, as cumulative effects could pose health risks to aquatic life and humans who consume fish.Environmental cadmium poisoning was confirmed as the source of a bone disease outbreak (itai-itai disease) in Japan during the late 1960s (Dural, M et al.2017).

Mercury is a highly poisonous heavy metal found in the environment. The general public is regularly exposed to mercury via consuming fish that may contain methyl mercury (CH3Hg) in their tissues, which is the most dangerous form of

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mercury (Squadrone S. et al.2018). This element exhibits strong bioaccumulation and biomagnification within the aquatic food chain. (US EPA 2021)

Arsenic exposure in the general population primarily occurs through the consumption of food and drinking water (Stancheva , M et al.2019). Only a small percentage of the overall arsenic content in fish exists in its inorganic form.Chronic exposure to inorganic arsenic can have a significant effect on both the peripheral and central nervous system.(Jarup, L.,2018) . Assessing the concentrations of toxic metals and comparing them with established criteria can help determine the potential health risks associated with consuming certain fish species. It is crucial to measure the levels of non-essential metals in fish to assess the potential dangers of consuming fish. This can be used as an indicator of the level of pollution in the coastal waters of Yemen.

METHOD

We gathered water and sediment samples from 9 sampling sites between 2022 and 2023. 81 samples of surface water, 81 samples of sediments, 108 samples of fish muscles, 108 samples of fish liver, and 108 samples of fish gills were collected and evaluated. Table (1) displays the dimensions and weight of the fish species that were gathered.

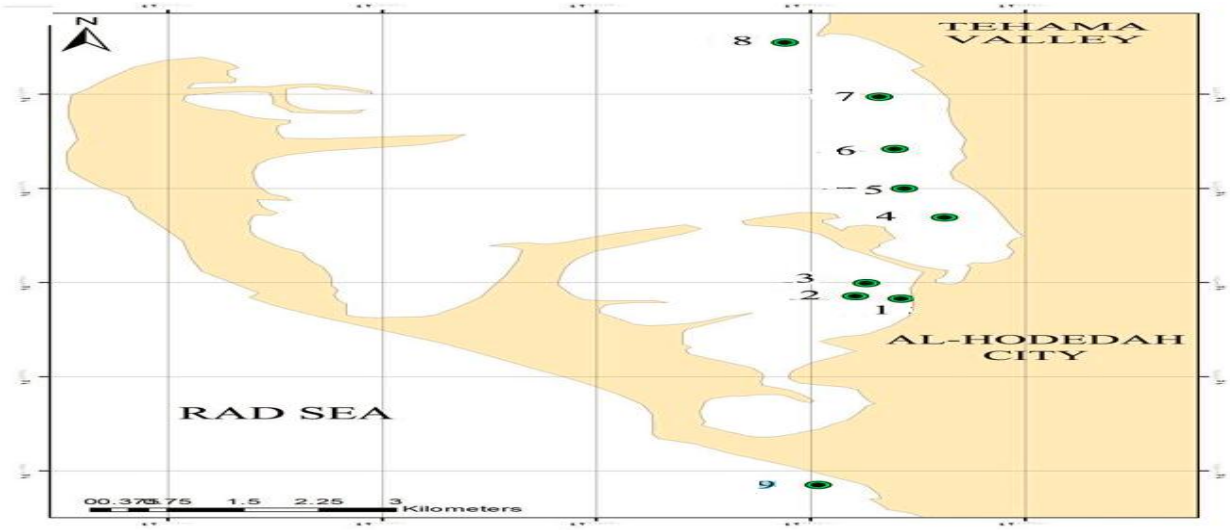

Fig. 1 Sampling locations (1–9) along the Coast of Al-Hodeidah, Yemen.

The samples of water were taken using a sanitized sampler. The samples were collected in 1-liter polyethylene bottles. All water samples were promptly taken to the laboratory and filtered using Whatman No. 41 filter paper with a pore size of 0.45 µm. The samples were acidified with 2ml of nitric acid to prevent metal precipitation, minimize adsorption onto container walls, inhibit microbial activity, and then stored at 4°C until chemical analysis. Water samples for mercury analysis are stored in a clean, airtight glass container that has been thoroughly cleansed prior to transportation (Tsuguyoshi, S. 2019). Water samples were obtained for arsenic analysis following Method 1632 (US EPA 2001). Water digestion for lead (Pb) and cadmium (Cd) analysis using graphite furnace atomic absorption spectrometry (GFAAS). Five milliliters of strong hydrochloric acid were applied to 250 ml of each surface water sample in a 600 ml beaker and then evaporated to a level of 25 ml. The concentrate was poured into a 50 ml volumetric flask and then diluted with deionized water up to the mark. Before analyzing, the solutions were passed through a Whatman No.41 filter paper with a pore size of 0.45 µm. Lead (Pb) and Cadmium (Cd) were tested using the Buck Model 210 VGP from the USA. Conducted analysis using a Graphite Furnace Atomic Absorption Spectrophotometer (GF AAS) on water samples prior to following Method 200.13.(US EPA 2001).

Water degradation for mercury (Hg) and arsenic (As) analysis using a hydride analyzer. 45 milliliters of surface water sample was measured.Each sample was treated with 5 ml of concentrated nitric acid (HNO_3, 65%) and 1 ml of concentrated hydrochloric acid (HCl, 35%). Ships Enclosed and positioned in microwave system. Specimens were heated based on time-pressure profiles. The vessels were cooled to room temperature, and then each sample was transferred to a final volume of 25 ml using deionized water. The sample may pose a safety risk. Pre-digest the sample in a fume hood with a loosely sealed vessel to allow gases to escape before continuing with Method 3015A. (US EPA 2007).

The Cold Vapor Hg Analyzer (Buck Model 410), manufactured in the United States, was utilized to analyze mercury levels in seawater samples, specifically suitable for EPA method 245.1. (Al-Shiwafi, N 2005). An Arsenic Hydride Analyzer (Buck Model 411), manufactured in the United States, was utilized to analyze arsenic in seawater samples, specifically suitable for EPA method 206.3. (CSBTS 1997)

The samples of sediment were gathered using a polyethylene corer following established protocols. The extraction of heavy metals followed the Standard Method 3051A, which involves microwave-assisted acid digestion of sediments as outlined by the US EPA.(US EPA 2007).

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A dry sediment sample weighing approximately 0.25 g was broken down using 6 ml of concentrated nitric acid (HNO3 65%), 1 ml of Perchloric acid (HClO4 65%), and 1 ml of hydrogen peroxide.30% hydrogen peroxide. Milestone Stard D Microwave Digestion Labstation equipped with an internal temperature sensor and a 260 terminal touch screen, featuring the HPR1000/10S High Pressure Segmented Rotor. Refer to Application Note HPR-EN-33. Microwave Schedule Two steps: (1) 15 minutes at 200 degrees and (2) another 15 minutes at 200 degrees. After Finish left containers for 20 minutes till they reached room temperature, the digested portion was diluted with deionized water to a final level of 50 ml (US EPA 2007) . Lead (Pb) and Cadmium (Cd) were analyzed without additional processing, while Mercury (Hg) and Arsenic (As) were diluted by a factor of 100.

Flame atomic absorption spectrometry (Buck Model 210 VGP) from the United States was utilized to analyze Cd and Pb in sediments, specifically suitable for EPA method 239.1. The values are 30 for Pb and 213.1 for Cd. A Cold Vapor Hg Analyzer (Buck Model 410) made in the U.S.A. was utilized to analyze mercury in sediments, specifically suitable for EPA method 245-5. An Arsenic Hydride Analyzer (Buck Model 411) made in the U.S.A. was utilized to analyze arsenic in sediments, specifically suitable for EPA method 206.3.(US EPA 2007).

The fish samples were rinsed with water that was deionized, placed in polyethylene bags, and stored in a freezer at -20°C until chemical analysis according to US EPA, 2000 guidelines (US EPA 2000). Fish tissues were dehydrated in an oven at 80°C until the sample reached a consistent weight. A dry tissue sample weighing approximately 0.500 g was digested using 7ml of concentrated nitric acid (HNO3 65%) and 1ml of hydrogen peroxide (H2O2 30%). The Milestone Start D Microwave Digestion Lab station features an integrated temperature sensor and a 260 terminal touch screen. Using HPR1000/10S High Pressure Segmented Rotor (Application Note HPR-FO-07) along with AOAC Official Methods 999.10 and 974.14. (AOAC 2010). Two-step microwave program: Step 1 - 15 minutes at 200 degrees, Step 2 - 15 minutes at 200 degrees. Allow the vessels to cool down to ambient temperature for 20 minutes. Then dilute the digested portion with deionized water to a final amount of 50 ml before continuing with Method 3052 (US EPA 1996). Lead was analyzed without additional processing, Cadmium was diluted by a factor of 2, and Mercury and Arsenic were diluted by a factor of 100. The Certified Reference Material DORM-2 was analyzed for its content of Pb, Cd, Hg, and As.

Graphite furnace atomic absorption spectrometry (Model 220 GF), manufactured in the United States, was utilized to analyze cadmium (Cd) and lead (Pb) levels in fish tissue samples, ideal for AOAC Official Method 999.10.A Cold Vapor Hg Analyzer (Buck Model 410), manufactured in the United States, was utilized to analyze mercury levels in fish tissue samples, specifically suitable for AOAC Official Method 974.14.35. An Arsenic Hydride Analyzer (Buck Model 411) made in the U.S.A. was utilized to analyze arsenic in fish tissue samples, specifically suitable for EPA method 206.3.(US EPA 2007). The table displays the dimensions and mass of the fish species that were gathered.

Table 1

The weight and length of fish collected from Al-Hodeidah coast, Red Sea of Yemen.

Specie Name (local name in Yemen)	No.	Habitat	Mean Total Length (range, cm)	Mean Fresh Weight (range, g)
Lethrinus mahsena (Gahash)	96	Demersal	30.99±6.321 (21.70- 38.00)	690.13±382.27 (184.16-1171.67)
Thunnus tonggol (Zainoop)	45	Pelagic	57.72±5.68 (51.00-67.10)	2544.42±729.88 (1761.88-3816.21)
Sphyraena jello (Kud)	60	Pelagic	49.01±6.64 (40.70-58.60)	778.40±304.95 (453.75-1213.67)
Epinephelus areolatus (Khulkhul)	75	Demersal	34.60±4.45 (27.90-40.00)	654.57±239.09 (331.18-986.55)

QUALITY ASSURANCE AND QUALITY CONTROL (QA/QC) PROCEDURES

Identical procedures were followed for preparing and treating both the blank samples and the regular samples. The concentrations were assessed by utilizing standard solutions produced in the identical acid matrix. Instrument calibration standards were established using mono-element certified reference solution (Buck). Reference fish samples (DORM-2) from the National Research Council Canada were utilized to verify the study. Metal recovery rates in all samples varied from 89% to 97%, as detailed in Appendix 1, Table 8. Recovery was evaluated by analyzing spiked samples at two different concentration levels. The recovery research data for fish, water, and sediment samples can be found in Appendix 1, table 9 and table 4. Recoveries ranging from 88% to 97% for spiked samples indicate the precision of the procedures employed.

STATISTICS

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One way ANOVA and two-way ANOVA techniques were used to assess for variations in the mean values of stations and seasons for significance (P ≤ 0.05) in all toxic metals data (lead, cadmium, mercury, and arsenic). Group means of environmental factors were evaluated using one-way ANOVA. Statistical analysis was conducted using Origin 9 and SPSS software, version 21.0.

RESULT & DISCUSSION

Toxic Metals in Water and sediment

Table 2 displays the levels of toxic metals found in water and sediment samples collected from the Al-Hodeidah location.

Table 2:
The average concentration of mean for Lead, Cadmium, Mercury and Arsenic in water (mg/L) and sediments (µg/g dry wt.) samples collected from Al-Hodeidah coast in Yemen.

Station number	Pb (mean±SD)		Cd(mean±SD)		Hg (mean±SD)		As (mean±SD)	
	Water	Sediment	Water	Sediment	Water	Sediment	Water	Sediment
1	0.053±0.001	76.028±2.493	0.007±0.002	2.381±1.072	0.007±0.002	0.023±0.009	0.007±0.002	0.097±0.012
2	0.053±0.001	75.883±2.424	0.007±0.002	2.384±1.05	0.007±0.002	0.022±0.01	0.008±0.002	0.097±0.011
3	0.055±0.005	76.041±2.531	0.008±0.002	2.380 ±1.087	0.007±0.002	0.022±0.01	0.008±0.002	0.097±0.011
4	0.098±0.005	76.504±2.143	0.008±0.001	2.396±0.993	0.006±0.001	0.028±0.015	0.009±0.001	0.109±0.012
5	0.105±0.017	76.708±2.309	0.007±0.001	2.397±0.966	0.007±0.001	0.028±0.016	0.009±0	0.109±0.012
6	0.105±0.014	76.628±2.151	0.008±0.001	2.400±0.952	0.007±0.001	0.028±0.016	0.009±0.001	0.109±0.012
7	0.081±0.014	77.042±3.563	0.006±0.001	2.489±0.368	0.008±0.001	0.011±0.004	0.008±0	0.091±0.028
8	0.083±0.015	77.059±3.569	0.006±0.001	2.493±0.343	0.008±0.001	0.012±0.003	0.008 ±0	0.092±0.027
9	0.084±0.015	76.987±3.528	0.006±0.001	2.495±0.367	0.008±0.001	0.012±0.003	0.008 ±0	0.091±0.027

The correlation coefficient (R) in Table (3) illustrates the relationship between the concentration of metals in water and sediment

Table 3:
Pearson's correlation coefficient (R) between Toxic metals level in water (mg/l) and sediment (µg/g dry wt.) samples collected from Al-Hodeidah coast in Yemen.

		Sediments			
		Pb	Cd	Hg	As
Water					
Pb	R	-0.042	0.020	0.260	0.058
Cd	R	0.194	-0.373	0.346	0.391*
Hg	R	-0.530**	-0.235	-0.025	0.150
As	R	0.221	0.414*	0.519**	0.347

The study revealed strong positive correlations between the concentration of Cd in the water and the As concentration in sediment at the same sites, with a correlation coefficient of + 0.391. A substantial negative correlation of -0.530 was established between mercury (Hg) levels in the water and lead (Pb) concentration in the sediments at the same sites. The Arsenic level in the water had strong positive correlations with the Cd and Hg amounts in the sediment, with correlation coefficients of +0.414 and +0.519, respectively (Table 3).

Toxic Metals bioaccumulation in fish tissues

Table 4 lists the quantities of lead, mercury, mercury ions, and arsenic in the muscle, liver, and gill of the four fish species

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(Lethrinus mahsena, Epinephelus areolatus, Thunnus tonggol, and Sphyraena jello). The gills of the fish species L. mahsena, T. tonggol, S. jello, and E. areolatus acquire the highest concentrations of Pb and Cd. The liver has the highest concentrations of mercury and arsenic.

Table 4

Lead, Cadmium, Mercury and Arsenic concentrations (µg/g dry wt.) in muscle, liver and gill of the fish samples collected from Al-Hodeida coast in Yemen.

Specie Name (local name in YEMEN)	Tissue	Mean Pb Concentration (range)	Mean Cd Concentration (range)	Mean Hg Concentration (range)	Mean As Concentration (range)
Lethrinus mahsena (Gahash)	muscle	0.194 ± 0.097 (0.076 - 0.357)	0.062 ± 0.018 (0.035 - 0.088)	0.057 ± 0.006 (0.049 – 0.068)	0.112 ± 0.006 (0.101 – 0.121)
	liver	0.694 ± 0.253 (0.293 - 0.999)	0.086 ± 0.014 (0.074 - 0.114)	0.091± 0.021 (0.070- 0.133)	0.122± 0.022 (0.090– 0.173)
	gill	0.962 ± 0.280 (0.696 - 1.466)	0.091 ± 0.012 (0.080 - 0.109)	0.019± 0.003 (0.014- 0.023)	0.035± 0.008 (0.024- 0.047)
Thunnus tonggol (Zainoop)	muscle	0.122 ± 0.036 (0.058 - 0.172)	0.037 ± 0.015 (0.019 - 0.065)	0.031 ± 0.009 (0.019 – 0.047)	0.076 ± 0.026 (0.044 – 0.117)
	liver	0.146 ± 0.033 (0.098 - 0.199)	0.088 ± 0.016 (0.067 - 0.107)	0.144± 0.034 (0.098– 0.186)	0.145± 0.030 (0.119– 0.198)
	gill	0.148 ± 0.029 (0.106 - 0.189)	0.236 ± 0.123 (0.095 - 0.433)	0.026± 0.008 (0.017- 0.044)	0.051± 0.016 (0.032- 0.074)
Sphyraena jello(Kud)	muscle	0.057 ± 0.018 (0.031 - 0.082)	0.031 ± 0.009 (0.018 - 0.045)	0.071 ± 0.006 (0.061 – 0.082)	0.093 ± 0.012 (0.069 – 0.112)
	liver	0.086 ± 0.026 (0.049 - 0.133)	0.092 ± 0.039 (0.047 - 0.157)	0.062 ± 0.007 (0.051- 0.071)	0.074± 0.006 (0.065- 0.084)
	gill	0.094 ± 0.020 (0.058 - 0.117)	0.109 ± 0.052 (0.057 - 0.206)	0.023± 0.006 (0.012- 0.033)	0.025± 0.007 (0.015- 0.034)
Epinephelus areolatus (Khulkhul)	muscle	0.179 ± 0.012 (0.163 - 0.198)	0.097 ± 0.036 (0.042 - 0.146)	0.068 ± 0.011 (0.051 – 0.082)	0.088 ± 0.012 (0.070 – 0.104)
	liver	0.184 ± 0.010 (0.166 - 0.200)	0.596 ± 0.074 (0.443 - 0.705)	0.126± 0.016 (0.101– 0.151)	0.137± 0.011 (0.118- 0.149)
	gill	0.143 ± 0.009 (0.131 - 0.159)	0.457 ± 0.198 (0.181 - 0.700)	0.011± 0.001 (0.009-0.012)	0.012± 0.001 (0.011- 0.013)

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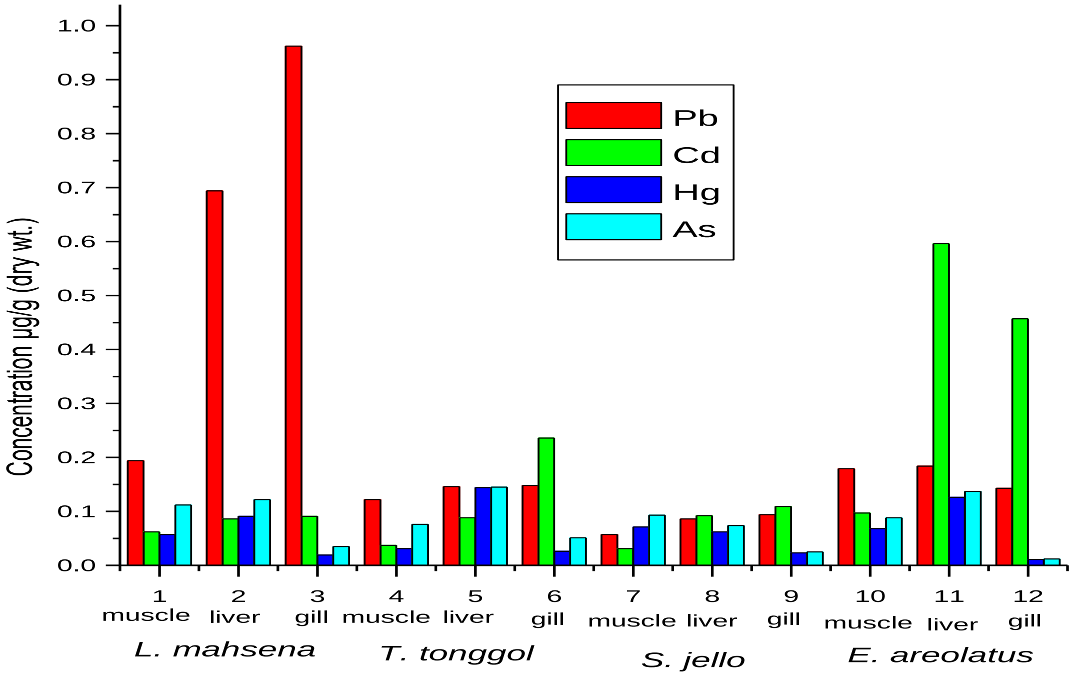

Fig. 2 Distribution of Toxic metals in in muscle, liver and gill of the fish samples collected from Al-Hodeida coast in Yemen.

Associations among Metal Concentrations in Tissues of Fish: Table (5) displays the correlation coefficient (r), which indicates the association between the concentrations of the four fish's selected tissues and the studied metals. There were positive correlations observed in muscle tissue between Cd and Pb with a correlation value of +0.624. Furthermore, Hg and Cd showed a positive correlation with a coefficient of + 0.390. Additionally, As content exhibited positive correlations with Pb, Cd, and Hg concentrations, with coefficients of +0.399, +0.399, and +0.472, respectively. There are positive correlations between the levels of As and Cd (+0.331) and between the levels of As and Hg (+0.887) in liver tissue. The gill tissue exhibited negative correlations between the levels of Cd and Pb (-0.357). Furthermore, a positive association was seen between As Levels and Hg concentrations in the gill tissue, with a correlation coefficient of +0.822 (Table 5).

Table 5

Interrelationships between toxic metals concentration with each other in the tissues of four fish species collected from Al-Hodeida coast in Yemen.

Tissue			Pb	Cd	Hg	As
Muscles	Pb	R	1	-	-	-
	Cd	R	0.624**	1	-	-
	Hg	R	-0.046	0.390*	1	-
	As	R	0.399*	0.339*	0.472**	1
Liver	Pb	R	1	-	-	-
	Cd	R	-0.202	1	-	-
	Hg	R	-0.176	0.325	1	-
	As	R	0.093	0.331*	0.887**	1
Gill	Pb	R	1	-	-	-
	Cd	R	-0.357*	1	-	-
	Hg	R	-0.065	-0.298	1	-
	As	R	0.173	-0.200	0.822**	1

Toxic Metals in Filtered Surface Water: The findings of the research indicated substantial differences in the concentration of mercury (Hg) and arsenic (As) in the filtered surface water, as determined by one-way ANOVA. Pb, Cd, and As tend to exhibit the highest concentration levels at stations 4, 5, and 6. This is likely caused by sewage discharge. Hg tends to have the maximum concentration at stations 7, 8, and 9. This is likely caused by the power stations located

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near the open side of Khor Al-Katheib. The elevated levels of Pb could be attributed to the petroleum-rich bedrock in the region.

One intriguing discovery suggests a positive linear correlation between Cd concentrations in filtered surface water and sediment levels (Table 3). This suggests that the source of Cd in filtered surface water may be from mineral weathering and chemical distribution and partitioning between the water and sediment.

The CSBTS, ANZECC, ARMCANZ, and ASEAN recommendations specify the maximum allowable levels of Lead, Cadmium, Mercury, and Arsenic in Seawater (Table 6). The levels of Lead and Mercury discovered above the allowable threshold. However, the levels of Cadmium and Arsenic measured are below the acceptable limit. The current elevated levels of lead (Pb) and mercury (Hg) may result from the petroleum-rich soil in the region. Oil contamination and deposition from the atmosphere could be causing the heightened concentrations.

The average levels of harmful metals fall within the limits set by global standards, as shown in Table 6. Human activity may have marginally polluted Stations 4, 5, and 6, making them the only exceptions. The Yemen shore in the present study has lower pollution levels compared to other regions.

Toxic Metals in Surface Sediments: Overall, using one-way and two ways ANOVA, the study's results demonstrated that there were significant differences ($P < 0.01$) in the sediments' concentrations of Pb, Cd, Hg, and As. The results in Table 2 show a significant difference. The variables that may contribute to pollution in the Red Sea include leaded gasoline, pollutant mobility, city wastewater discharge, Red Sea's physical properties, port effluents, industrial pollution, rainfall, municipal runoffs, atmospheric deposition, and oil enrichment in nearby areas.

The quantities of metals in the sediments align well with international regulations, as shown in Table 7. The elevated levels of metals in the sediments compared to water may result from causes such as pollutant transportation, city wastewater discharge, Red Sea's physical properties, and effluents from Al-Hodeidah landing port (ASEAN Marine Water Quality 2008). The average levels of harmful metals fall within the range of values found in other studies (Table 7).

Table 7

Comparison between mean concentrations of toxic metals in the sediment from Al-Hodeidah coast with international regulations (µg/g) dry weight.

Location	Pb	Cd	Hg	As	Reference
Al-Hodeidah Coast of Yemen	75.88-77.05	2.380-2.495	0.011-0.028	0.091-0.109	Present study
CCME (ISQG – PEL)	30.2 - 112.0	0.70 – 4.20	0.130 – 0.700	7.24– 41.6	FAO/ WHO, 2023
ANZECC and ARMCANZ (ISQG-Low to ISQG-High)	50.0 – 220.0	1.50 – 10.0	0.15 – 1.0	20.0 – 70.0	Qadir A et al.2019

Relationships between metals concentration in water and sediment: A noteworthy discovery reveals positive linear correlations between the levels of lead in filtered surface water and sediments (Table 3). This suggests that the source of the lead in the filtered surface water may be mineral weathering, as well as chemical distribution and partitioning between the sediment and water. These results align with those acquired by (CCME 1999). Possible sources of these metals in the coastal area may involve air deposition, dredging activities, direct disposal, and sewage sludge. The physical processes and prevailing orientation could influence the specific distribution of these metals along the Yemeni coastline area. Contaminated particle or sediment is distributed throughout an ecosystem, mixing with water, detritus, and living organisms, leading to continuous pollution of all environmental areas. (Pyle GG, Rajotte JW, Couture P (2015). The positive association shown between the metal concentration in the water and sediment in Table 3 of the current investigation reinforces this claim.

Toxic metals bioaccumulation in fish tissues: Gills acquire the highest levels of lead and copper in all of the fish species under investigation, including L. mahsena, T. tonggol, S. jello, and E. areolatus. The gill has shown the highest concentration of metals compared to other organs. The liver has the highest concentrations of mercury and arsenic. The liver is the primary organ responsible for detoxification, where various toxic substances acquired from the environment are processed and neutralized. Research conducted on many fish species has demonstrated that heavy metals primarily concentrate in the metabolically active liver, where they are stored and detoxified through the production of metallothioneins. (Carpene E 2019). Metallothioneins (MTs) are low molecular weight proteins rich in cysteine that can bind to both physiological and xenobiotic heavy metals using the thiol group of cysteine. The elevated concentrations of trace elements in the liver compared to other tissues are due to the strong binding between MT proteins and these heavy elements. (Khaled, A 2020)

In comparison to the liver and gills, the muscle of every fish species studied in this study has been found to accumulate fewer metals. Muscle tissue is not a primary location for metal buildup (Khaled, A 2020). Cadmium and lead lack a biological function and are therefore detrimental to living organisms even at relatively low levels. The study revealed that T. tonggol and S. jello had metal concentrations in the order of Pb > Cd > As > Hg, while L. mahsena had metal concentrations in the order of Pb > As > Cd > Hg. However, in the case of E.areolatus fish species, metal concentrations were in the order of Cd > Pb > As > Hg. The results aligned with the findings of (Bahnasawy, M et al.2019) (Pb > Hg > Cd > As), but this is not always the case. Fish muscle is not a tissue that actively accumulates heavy metals (Asante, F et al.2021). The current study focused on the levels of heavy metals in fish muscles, as this part is the most commonly ingested by the Yemeni population. Additionally, it has been recorded that fish in contaminated areas can collect high quantities of metals in their tissues, sometimes above the maximum allowed limits.

The sequence of lead accumulation in several organs was L. mahsena > E. areolatus > T. tonggol > S. jello. The overall ranking showed that L. mahsena accumulated the highest concentration of heavy metals among the four fish species, suggesting that this species has a greater capacity to accumulate these metals in its liver and gills. Their dietary patterns, lipid content, and excretion rate may influence the presence of hazardous metals in fish tissue. The order of Cadmium and Mercury accumulation in different organs is E. areolatus > T. tonggol > L. mahsena > S. jello. The current elevated levels of cadmium (Cd) and mercury (Hg) in E. areolatus and the high concentration of lead (Pb) in L. mahsena are commonly linked to their natural environment and dietary habits. E. areolatus and L. mahsena typically inhabit the same area.47 Lipid content in the tissue and excretion percentage of hazardous metals from the body could explain this phenomenon (Abdul-Wahab , S et al.2022).

Organ-specific arsenic accumulation revealed the following hierarchy: T. tonggol > L. mahsena > E. areolatus > S. jello. The current elevated level of Arsenic in T. tonggol could be due to factors such as eating habits, species, age and size of fish, bioavailability of chemicals in food and water, exposure duration, and bioaccumulation (Saei-Dehkordi, S. S et al.2019). The rise in As levels may be due to variations in metabolism (Qadir A., and Malik R 2019) . In the polluted fish, the order of Pb and Cd accumulation in tissues was gill > liver > muscle, while for Hg and As it was liver > muscle > gill (Table 4). Luoma SN (2018) reported comparable findings of elevated levels of lead (Pb) and cadmium (Cd) in gills. Fish gills containing high levels of lead and mercury could be the consequence of water contaminated by pollutants in the environment. The variation in results may be attributed to factors such as anthropogenic activities, feeding habit of fish species, fat content in their food, and changes in local pollutants. The average levels of harmful metals in fish tissues fall within the reported range from other sources.

Relationships between metals concentration in fish tissues: A significant association (r = 0.624) exists between Cd and Pb levels in muscles, as seen in Table 5. Metal interactions are crucial in influencing the bioavailability and toxicity to fish in an aquatic environment. Positive correlations in our data show that certain heavy metals in the muscles share distribution features or may imply comparable contamination levels or come from the same pollution source. (Rogers, J. T. and Wood, C. M 2021). The data in Table 5 show a strong positive connection between arsenic (As) and mercury (Hg) levels in the liver. Due to the bioaccumulation of harmful heavy metals in fish tissues (Rogers, J. T. and Wood, C. M 2021). The results align with previous findings that fish can absorb Pb and Cd through the gills' Ca^{2+} uptake pathways, potentially competing for uptake sites. This competition results in an inverse relationship between the two metals at the gill uptake sites, consistent with the negative correlation observed in our data (table 5) between Pb and Cd in gill tissues.

Toxic Metal Concentrations vs. International dietary Standards and Guidelines. The maximum allowable limit of lead in fish is set by the FAO/WHO (2023) and Yemen Standardization (2013) as 0.3 and 1.00 µg/g (dry weight). The highest concentrations of lead in the muscles, livers, and gills of the four fish species investigated were 0.194 ± 0.097 µg/g dry wt., 0.694 ± 0.253 µg/g dry wt., and 0.962 ± 0.280 µg/g dry wt., respectively, in L. mahsena. The levels of Pb found in the muscles, livers, and gills were within the safe limit of 1.0 µg/g dry wt. set by the Standard Specification for Yemen for food fish (Commission Regulation (EC) 2023). The FAO/WHO recommendations specify the maximum allowable limit of Lead in Fish as 0.3 µg/g (dry wt.). The levels of Lead found in the livers and gills of L. mahsena fish above the allowed limit.

The maximum allowable level of cadmium in fish is set by the Yemen Standardization (2013) and the European Community (2023) at 0.20 and 0.10 µg/g dry weight, respectively. In E. areolatus, the highest concentrations of Cadmium were found in the muscles (0.097 ± 0.036 µg/g dry wt.), livers (0.596 ± 0.074 µg/g dry wt.), and gills (0.457 ± 0.198 µg/g dry wt.) among the four examined fish species. The Cd levels in the muscles were below the safe limit of 0.10 µg/g (dry wt.) set for food fish by the EC (Commission Regulation (EC) 2023) . The levels of Cadmium found in the livers and gills of E. areolatus fish above the allowable limit.

According to Yemen Standardization rules and the FAO/WHO, the maximum acceptable value of Mercury in Fish is 0.50 µg/g dry wt. The highest concentrations of mercury in the muscles, livers, and gills of the four fish species investigated were 0.071 ± 0.006 µg/g dry weight in S. jello and 0.144 ± 0.034 µg/g dry weight in T. tonggol, respectively. The observed Mercury levels were within the permitted limits set by FAO/WHO and Yemen Standardization (2013).

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The FAO/WHO and Yemen Standardization recommendations specify a maximum allowable level of Arsenic in Fish as 0.10 µg/g dry wt. and 1.0 µg/g dry wt. respectively. In the muscles, livers, and gills of the four fish species studied, the maximum concentration of arsenic was found in T. tonggol at 0.112 ± 0.006 µg/g dry weights in L. mahsena, 0.145 ± 0.030 µg/g dry weights, and 0.051 ± 0.016 µg/g dry weights, respectively. The permissible limit of 1.0 µg/g (dry wt.) set by the Yemen Standardization for food fish was not exceeded by the levels of As found in the muscles, livers, and gills. The permissible limit of 1.0 µg/g (dry wt.) set by the Yemen Standardization for food fish was not exceeded by the levels of As found in the muscles, livers, and gills. The levels of Arsenic found in the muscles of L. mahsena and the livers of T. tonggol fish above the allowed limit

CONCLUSION

The study revealed that harmful metals in sediments around the Al-Hodeidah shoreline surpassed global criteria, although lead and mercury levels above tolerable limits. The metals caused slight pollution in the area, particularly close to sewage outlets and power plants. The contamination is partially due to pollutants entering the atmosphere from motor vehicles and mountainous areas. Metals were found to be more concentrated in the liver and gills of fish, with varying quantities among different metals. Variances in heavy metal distribution can be attributed to aspects like behavior, food patterns, habitats, ecological requirements, metabolism, biology, physiology, and regulatory capacity. Various parameters, including length, weight, water quality, sex, and size, can also affect the accumulation of metals in organisms. The metal contents in four species were either lower or fell within the concentration limits observed in Red Sea fishes. The concentrations of Pb, Cd, Hg, and As in the muscle of each species were analyzed and found to be within safe limits for human consumption. Toxic metal pollution in Al-Hodeidah seashore remains isolated and is similar to levels found in other regions globally. Hence, strict inspection measure must be taken in connection with human health as the above four fish species have a great commercial importance in Yemen. We advocate implementing a continual monitoring program for the Red Sea coast of Yemen to maintain its cleanliness and prevent contamination in the foreseeable future.

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REFERENCES

1. Abdel-Baki, A. S. ; Dkhil, M. A. and Al-Quraishy, S. Bioaccumulation of some heavy metals in tilapia fish relevant to their concentration in water and sediment of WadiHanifah, Saudi Arabia. African J of Biotechnology, 2011; 10(1): 2541-2547.
2. Belin, S.; Sany, T. and Salleh, A. Heavy metal contamination in water and sediment of the Port Klang coastal area , Selangor , Malaysia, (2018) (1):2013–2025
3. Wu, Y. and Chen, J. investigating the effects of point source and nonpoint source pollution on the water quality of the East River (Dongjiang) in South China. Ecological Indicators, 2018; 32(1):294–304.
4. Varol, M.; and Şen, B. Assessment of nutrient and heavy metal contamination in surface water and sediments of the upper Tigris River, Turkey. CATENA, 2017; 92(1):1–10.
5. Wang, C.; Niu, Z.; Li, Y.; Sun, J. and Wang, F. Study on heavy metal concentrations in river sediment through the total amount evaluation method. J. Zhejiang Univ.-Sci. A (Appl. Phys. and Eng.) 2021; 12(5):399-404
6. Schulz, U. H. and Martins-Junior, H. Astyanafaseiatus as bio indicator of water pollution of Rio Dos Sinos, Rs, Brazil. Braz. J. Biol, 2001; 61(4):615-622
7. Mason, L. H.; Harp, J. P.; and Han, D. Y. (2014). Pb Neurotoxicity: neuropsychological effects of lead toxicity. Biomed. Res. Int.; Vol. 2014
8. Dural, M.; Goksu, L. M. and Ozak, A. A. Investigation of heavy metal levels in economically important fish species captured from the Tuzla lagoon. Food Chemistry, 2017; 102(1):415-421.
9. S. Squadrone, M. Prearo, P. Brizio, S. Gavinelli, M. Pellegrino, T. Scanzio, S. Guarise, A. Benedetto, M.C. Abete. Heavy metals distribution in muscle, liver, kidney and gill of European catfish (Silurus glanis) from Italian Rivers , Chemosphere 90 (2018), 358–365
10. Stancheva , M. Makedonski, L. And Petrova, E. DETERMINATION OF HEAVY METALS (Pb, Cd, As AND Hg) IN BLACK SEA GREY MULLET (MUGIL CEPHALUS), Bulgarian Journal of Agricultural Science, 19 (Supplement 1) 2019, 30–34.
11. FAO/WHO, 2023. Summary of Evaluations Performed by the Joint FAO/WHO Expert Committee on Food Additives (JECFA 1050-2023), ILSI Press International Life Sciences Institute 2023.
12. Jarup, L., 2018. Hazards of heavy metal contamination. British Medical Bulletin, 68:167–182.
13. Tsuguyoshi, S. (2019). Mercury Analysis Manual. Ministry of the Environment, Japan.

E-ISSN : 2962-1658
Volume 3, Number 1, June, 2024
https://doi.org/10.47709/ijmdsa.vxix.xxxx

14. US EPA. Method 1632: Chemical Speciation of Arsenic in Water and Tissue by Hydride Generation Quartz Furnace Atomic Absorption Spectrometry. Washington, D.C.: U.S. Environmental Protection Agency (2001).
15. US EPA. Method 200.13: Determination of Trace Elements in Marine Waters by Off-Line Chelation Preconcentration with Graphite Furnace Atomic Absorption. Washington, D.C.: U.S. Environmental Protection Agency (2017).
16. US EPA. Method 3015a Microwave assisted acid digestion of aqueous samples and extracts. Washington, D.C.: U.S. Environmental Protection Agency (2007).
17. US EPA. Method 245.1, Revision 12: Determination of Mercury in Water by Cold Vapor Atomic Absorption Spectrometry. Washington, D.C.: U.S. Environmental Protection Agency (2021).
18. US EPA. Method 206.3 Arsenic (AA, Gaseous-Hydride). Washington, D.C.: U.S. Environmental Protection Agency (2007).
19. US EPA. Method 3051A Microwave assisted acid digestion of sediments, sludge, soils, and oils. Washington, D.C.: U.S. Environmental Protection Agency (2007).
20. US EPA. Method 239.1 Lead (AA, Direct Aspiration). Washington, D.C.: U.S. Environmental Protection Agency (2001).
21. US EPA. Method 213.1 Cadmium (AA, Direct Aspiration). Washington, D.C.: U.S. Environmental Protection Agency (2001).
22. US EPA. Method 245.5 Mercury in Sediments by Manual Cold Vapor Atomic Absorption (CVAA). Washington, D.C.: U.S. Environmental Protection Agency (2011).
23. US EPA. Environmental Protection Agency Chemical Contaminant Data for Use in Fish Advisories Vol. 1 Fish Sampling and Analysis Third Edition. Washington, DC: Office of Science and Technology (2000).
24. AOAC, Association of Official Analytical Chemists: Official Method 974.14. Mercury in Fish, first action 1974. NMKL-AOAC method, Washington, DC, USA, 18th edition, Revision 3, 2010.
25. US EPA. Method 3052 microwave assisted acid digestion of siliceous and organically based matrices. Washington, D.C.: U.S. Environmental Protection Agency (1996).
26. Al-Shiwafi, N.; Rushdi, A. I. and Ba-Issa, A., Trace metals in surface seawaters and sediments from various habitats of the Red Sea coast of Yemen, Environ Geol, 48 (2005): 590–598
27. CSBTS (China State Bureau of Quality and Technical Supervision). 1997. The People's Republic of China National Standards Seawater Quality Standards (GB 3097-1997), Standards Press of China, Beijing (in Chinese).
28. ASEAN Marine Water Quality: Management Guidelines and Monitoring Manual. First Edition. 2008. Australia: New Millennium Pty Ltd. Print.
29. CCME, Canadian Council of Ministers of the Environment (2002). Canadian Sediment Quality Guidelines for the Protection of Aquatic Life. Summary Tables. Update 2002. In: Canadian environmental quality guidelines, 1999, Canadian Council of Ministers of the Environment, Winnipeg.
30. Pyle GG, Rajotte JW, Couture P (2015) Effects of industrial metals on wild fish populations along a metal contamination gradient. Ecotoxicol Environ Saf 61(3):287-312.
31. Carpene E, Vasak M. Hepatic Metallothionein from Goldfish (Carassius auratus). Comp Biochem Physiol; Vol.92B(2019):463-468
32. Ikem, A.; Egiebor, N. O. and Nyavor, K. Trace Elements in Water, Fish and Sediment from Tuskegee Lake, Southeastern USA. Water, Air, and Soil Pollution, 149(2018): 51–75
33. Khaled, A. Heavy metals concentrations in certain tissues of fivecommercially important fishes from El-Mex Bay, Alexandria, Egypt. Egyptian Journal of Aquatic Biology and Fisheries, 8(1) (2020): 51-64.
34. Bahnasawy, M.; Khidr, A. and Dheina, N. Seasonal Variations of Heavy Metals Concentrations in Mullet, MugilCephalus and Liza Ramada (Mugilidae) from Lake Manzala, Egypt. Journal of Applied Sciences Research; 5(2019):845-852.
35. Asante, F.; Agbeko, E.; Addae, G and Quainoo, A. K, Bioaccumulation of Heavy Metals in Water, Sediments and Tissues of Some Selected Fishes from the Red Volta, Nangodi in the Upper East Region of Ghana, British Journal of Applied Science & Technology, 4(4):(2021): 594-603
36. Abdul-Wahab , S.; Al-Husaini, I.; Rahmalan, A.: Using grouper fish as bio-indicator of Cd, Cu, Pb and V in the vicinity of a single buoy mooring (SBM3) at Mina Al Fahal in the Sultanate of Oman. Bull Environ. Contam. Toxicol, 91(2022): 684–688.
37. Saei-Dehkordi, S. S.; Fallah, A. A. and Nematollahi, A. Arsenic and mercury in commercially valuable fish species from the Persian Gulf: influence of season and habitat, Food Chem. Toxicol. 48(2019): 2945-2950.
38. Qadir A., and Malik R., Heavy metals in eight edible fish species from two polluted tributaries (Aik and Palkhu) of the River Chenab. Pakistan, Biol Trace Elem Res., 143, (2019):1524-1540.
39. Luoma SN. Bioavailability of trace metals to aquatic organisms- a review Sci.Total Environ. 28 (2018): 1-12.
40. Rogers, J. T. and Wood, C. M. Characterization of branchial lead-calcium interaction in the freshwater rainbow trout *Oncorhynchus mykiss.* J. Exp. Biol. 207(2021):813-825.

E-ISSN : 2962-1658
Volume 3, Number 1, June, 2024
https://doi.org/10.47709/ijmdsa.vxix.xxxx

41. FAO/ WHO, 2023. Safety evaluation of certain contaminants in Food, Safety evaluation of certain contaminants in food / prepared by the Seventy-second meeting of the Joint FAO/WHO Expert Committee on Food Additives (JECFA). https://creativecommons.org/licenses/by-nc-sa/3.0/igo
42. Yemen Standardization, Metrology and Quality Control. Fish and fish products, fresh fish. The Republic of Yemen. 2013; 1577:1-9.
43. Commission Regulation (EC) 2023/915 of 25 April 2023 on maximum levels for certain contaminants in food and repealing Regulation (EC) No 1881/2006 https://eur-lex.europa.eu/eli/reg/2023/915/oj

APPENDIX

Table (8)

Analytical results (in µg g^{-1}) of certified reference material DORM-2 (Dogfish muscle and liver, National Research Council Canada), showing local laboratory values and recommended values

Element	Measured value (Mean±SD)	n	Certified value (Mean±SD)	% recovery
Lead	0.058 ±0.002	6	0.065 ±0.007	89
Cadmium	0.040 ±0.005	6	0.043 ±0.008	93
Mercury	4.39 ±0.18	6	4.64 ±0.26	95
Arsenic	15.84±0.70	6	16.4±1.10	97

Table (9)

Percentage recovery of detected heavy metals in the muscles of *Thunnus tonggol* and *Epinephelus areolatus* sample

Toxic metals	Unspiked concentration (µg/g)	Sample Name	Added amount(mg/l)	Spiked concentration (µg/g)	% recovery
Lead	0.129	*Thunnus tonggol* (0.5g)	0.05	0.175	92
	0.123	*Epinephelus areolatus* (0.5g)	0.07	0.186	90
Cadmium	0.030	*Thunnus tonggol* (0.5g)	0.02	0.049	95
	0.097	*Epinephelus areolatus* (0.5g)	0.05	0.144	94
Mercury	0.021	*Thunnus tonggol* (0.5g)	0.01	0.030	90
	0.051	*Epinephelus areolatus* (0.5g)	0.02	0.069	90
Arsenic	0.091	*Thunnus tonggol* (0.5g)	0.04	0.129	95
	0.104	*Epinephelus areolatus* (0.5g)	0.05	0.151	94