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A Risk-Benefit Analysis for Human Consumption Due to Essential and Toxic Metals in Marine Organisms of Albania

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Abstract

Trace elements naturally occur in marine ecosystems, with some playing vital roles in biological processes, while others pose toxicological risks to humans and marine organisms. This study presents a comprehensive evaluation of essential and trace metals (Fe, Zn, Cu, Cr, Mn, Ca, Mg) in edible and non-edible tissues of marine species collected along the Albanian coastline. Concentrations were analyzed to assess nutritional benefits, pollution levels, and potential human health risks using indicators such as Estimated Daily Intake (EDI), Target Hazard Quotient (THQ), Hazard Index (HI) and cluster analysis. Results revealed that most species are nutritionally beneficial and safe for consumption, with metal concentrations generally below safety thresholds. However, higher concentrations in liver and gill tissues indicate tissue-specific bioaccumulation. Cluster analysis highlighted differences in metal profiles by species and tissue type, aiding in source discrimination and future monitoring. Overall, the findings support the consumption of Albanian marine species while emphasizing the importance of monitoring specific metals and organs.

Keywords

Trace Elements, Marine Biota, Albania, Toxicity, Essentiality, Seafood Safety, SAA, Risk Assessment

1. Introduction

Trace elements are ubiquitous in marine environments, introduced via both natural processes and anthropogenic activities [1] [2]. While elements such as zinc (Zn), copper (Cu), iron (Fe), selenium (Se), calcium (Ca), and magnesium (Mg) are essential micronutrients required for physiological functions [3] [4], others like cadmium (Cd), lead (Pb), mercury (Hg), and arsenic (As) are toxic even at low concentrations [5] [6]. The accumulation of these elements in edible marine organisms raises concerns about food safety, especially in regions with increasing coastal development and pollution, such as Albania [7] [8]. Marine organisms such as fish, molluscs, crustaceans, and marine mammals serve as indicators of environmental contamination, and their analysis provides insight into the health of marine ecosystems [9] [10]. Understanding the balance between essential and toxic metal concentrations in marine biota is crucial for environmental monitoring, regulatory assessments, and public health protection [11] [12]. Essential metals support various physiological functions in humans. For example, iron is vital for oxygen transport in blood; zinc and copper play roles in immune function and enzyme regulation; selenium has antioxidant properties, while magnesium supports muscle and nerve function [13]-[15]. Even essential elements can become toxic to living organisms when their concentrations exceed certain thresholds.

While trace metals like iron (Fe), copper (Cu), zinc (Zn), and manganese (Mn) play vital roles in enzymatic reactions, oxygen transport, and antioxidant defence, excessive accumulation disrupts cellular homeostasis and induces oxidative stress, cytotoxicity, and organ dysfunction [16]. For instance, excess iron promotes the Fenton reaction, generating reactive oxygen species (ROS) that damage lipids, proteins, and DNA [17]; Copper (Cu) is toxic at high levels, leading to liver damage and neurological disorders due to oxidative stress and protein misfolding [18]; Zinc (Zn) in excess interferes with the absorption of other essential elements like iron and copper and can suppress immune responses [19]; Manganese (Mn) chronic overexposure, particularly via inhalation or contaminated water, is neurotoxic and linked to Parkinsonian symptoms [20].

In contrast, elements such as mercury (Hg), cadmium (Cd), lead (Pb), and arsenic (As) are non-essential and toxic even in trace amounts [4] [5]. These metals may enter marine food chains through industrial discharge, mining, agricultural runoff, or natural geological processes [2] [7]. Marine species—particularly large predatory fish like tuna and swordfish—can accumulate these contaminants to levels that pose serious health concerns for humans, including neurotoxicity (e.g., from methylmercury exposure), [16]; renal dysfunction (e.g., from cadmium [17]; developmental and reproductive toxicity; carcinogenic effects (notably from inorganic arsenic and lead) [18]-[20].

High concentrations of metals found in marine biota have been reported around the world. For example, Storelli *et al.* (2002) [10] reported 5.5 mg/kg ww of Hg in tuna and swordfish; Van der Oost *et al.* (2003) [21] reported 9.1 mg/kg ww of Cd in mussels and cephalopods; [19] reported 3.4 mg/kg ww Pb in shellfish and crabs; Neff (1997) [22], reported 100 mg/kg ww As in bivalves and demersal fish; Tuzen (2003) [23], reported 5.6 mg/kg ww Ni in shrimps and mussels.

In marine biota, heavy metals bind to various biomolecules—especially proteins, lipids, and carbohydrates—through mechanisms that reflect both the organism's detoxification pathways and the metal's chemical nature [24] [25]. Understanding these binding interactions is critical for assessing metal bioavailability, ecotoxicological risks, and human dietary exposure through seafood consumption. Metals such as Cu, Zn, and Fe often bind to metalloproteins (e.g., hemocyanin, ferritin) and enzymes, where they serve functional roles. For example, Zn can be a cofactor in enzymes like carbonic anhydrase [14]. Metallothioneins are low-molecular-weight, cysteine-rich proteins that bind metals such as Cd, Hg, Zn, and Cu, acting as a detoxification and regulation mechanism [14] [15]. Metallothioneins sequester metals in a non-toxic form and are key biomarkers of metal exposure.

Some metals, particularly lipophilic organometallic compounds like methylmercury (MeHg), can integrate into phospholipid bilayers, disrupting cellular function [16]. MeHg binds strongly to thiol (-SH) groups in membrane and tissue proteins. Methylmercury in fish is particularly dangerous due to its high assimilation and long biological half-life (up to 70 days) in humans [26]. Carbohydrates and mucopolysaccharides containing negatively charged groups (e.g., carboxyl or sulfate) on polysaccharides in the extracellular matrix, mucus, or exoskeletons (e.g., chitin in crustaceans) can bind positively charged metal ions [27]. In some cases, metals such as Pb and Hg may interact with DNA or RNA, interfering with transcription and replication, leading to genotoxic effects [28]. Metals may associate with negatively charged sites on cell surfaces (e.g., phosphate groups or amino acids like glutamate and aspartate). If we consider the mechanisms on which metals can bind in fish organisms, most known ways account for ionic binding (electrostatic attraction); covalent or coordinate bonding: metals like Hg and Cd form strong coordinate covalent bonds with thiol (-SH) groups, especially in cysteine residues of proteins; chelation (biota may use natural chelators (e.g., phytochelatins, metallothioneins) to bind and detoxify metals; adsorption to external surfaces - some metals remain loosely bound to the outer shell, gills, or surface tissues, especially in mollusks or crustaceans, and may not represent true bioaccumulation [1] [12]. Among the factors that affect binding of metals in living organisms we can mention species-specific metabolism; age and trophic level; environmental parameters such as pH, salinity, and dissolved organic matter; and chemical form of the metal (e.g., inorganic vs. organic mercury) [1] [22]. The assimilation of metals from seafood consumption ranges from less than 10% to over 90%, depending on the metal form [29]. The most concerning from a public health perspective is methylmercury, due to its high absorption and toxicity, especially for pregnant women and children [26]. Conversely, essential metals like selenium and zinc in fish offer nutritional benefits when consumed within recommended dietary limits [11]. In **Table 1** below, the typical absorption rate of HM from sea food consumption is presented.

Some metals become more bioavailable in the acidic gastric environment—such as cadmium (Cd) and lead (Pb)—due to increased solubility [30]. Metals cross the intestinal wall via various mechanisms: passive diffusion for small, lipophilic compounds like methylmercury (MeHg) [16]; facilitated transport using shared pathways with essential nutrients like Fe^{2+}, Ca^{2+}, and Zn^{2+} [31]; and endocytosis or active transport for some protein-bound forms [16] [31]. Once absorbed into the bloodstream, metals bind to plasma proteins such as albumin and transferrin, facilitating distribution to target organs [16].

Table 1. Typical assimilation rate of metals.

Metal	Typical Assimilation (Absorption) Rate	Notes
Iron (Fe)	10% - 20%	Non-heme iron in fish is less bioavailable than in meat. Enhanced by vitamin C.
Zinc (Zn)	20% - 40%	Higher in fish and shellfish; influenced by dietary phytates.
Copper (Cu)	30% - 50%	Essential cofactor; well absorbed from marine proteins.
Manganese (Mn)	3% - 10%	Low absorption; regulated by homeostasis.
Selenium (Se)	80% - 90%	Very high bioavailability from fish (especially as Selenomethionine).
Magnesium (Mg)	30% - 50%	Found in bones and tissues; highly bioavailable.
Inorganic Mercury (Hg^{2+})	<10%	Poorly absorbed compared to MeHg.
Cadmium (Cd)	5% - 15%	Absorption increases with iron deficiency or low Calcium intake.
Lead (Pb)	10% - 15% (adults) up to 50% (children)	More readily absorbed in children; stored in bones.
Nickel (Ni)	1% - 10%	Limited absorption from food.

Due to these concerns, international bodies such as the World Health Organization (WHO), European Food Safety Authority (EFSA), and Codex Alimentarius Commission have established maximum permissible limits for heavy metals in seafood to protect consumers.

In conclusion, while marine biota are valuable components of a healthy diet, the presence of heavy metals—both essential and toxic—requires ongoing surveillance. Risk assessments and regulatory controls are essential to ensure that seafood remains a safe and beneficial part of human nutrition.

Albania's coastline along the Adriatic and Ionian Seas is rich in biodiversity and supports a variety of commercial fisheries. Despite this, limited data exist on the trace element composition of its marine biota. This study aims to fill that gap by assessing the essentiality and toxicity of trace elements in edible species and evaluating associated health risks for consumers.

2. Materials and Methods

2.1. Sample Collection and Treatment

Accurate determination of metals in marine biota requires meticulous sample preparation and strict quality control to prevent contamination and ensure data reliability. Samples were collected in different coastal areas in Albania, respectively in the fish market of Vlora, Saranda, Divjaka, Fieri (Seman coast) and Lezha cities.

Just one sample belongs to lake water, respectively *Cyprinus carpio*, collected at Pogradeci city. Samples that exceed 1 kg are labelled, while the weight of the rest of the species was below 1 kg. In this study, except for the tissue, where it was possible the liver, eggs and gills were also analysed. A table summarizing the name of the species and location of collection is presented below. Upon collection, samples such as muscle tissues, soft organs, or whole organisms are thoroughly rinsed with deionized water to remove adhering sediments and external contaminants. Collected samples represent big species, having a high body mass. Respectively, selected fish species have a body mass, ranging from 2.0 - 10 kg. Samples were homogenized, using acid-washed stainless steel blender, and stored at −20˚C prior to digestion. Wet digestion was performed using concentrated nitric acid (HNO_3), in closed Teflon vessels for an efficient and complete mineralization of organic matrices.

Table 2. Summary of species and their location of sampling.

Name of species	Analysed body part
Merluccius merluccius, V	Tissue, eggs, gills
Pagellus erythrinus, V	Tissue, liver, gills
Dicentrarchus labrax, 5 kg, V	Tissue, gills
Thunnus thynnus muscle, 10 kg, V	Tissue, liver, gills
Conger conger, Vlore	Tissue
Loligo vulgaris, V	Tissue
Dentex dentex, V	Tissue
Dicentrarchus labrax, V	Tissue
Sepia officinalis (big one), V	Tissue
Dicentrarchus labrax 5 kg, V	Tissue, gills
Parapenaeus longirostris, V	Tissue
Dicentrarchus labrax, S	Tissue, gills
Sparus aurata, S	Tissue, eggs, gills
Pagellus erythrinus, 1.5 kg, S	Tissue, gills
Dicentrarchus labrax, DI	Tissue
Solea sp., DI	Tissue
Mugil cephalus, DI	Tissue
Sparus aurata, DI	Tissue
Parapenaeus longirostris, DI	Tissue
Sparus aurata, SE	Tissue
Dentex dentex, LE	Tissue
Cyprinus carpio, P	Tissue

To ensure accuracy and reproducibility, certified reference materials (CRMs) such as fish tissue (e.g., IAEA 407 Trace elements and MeHg in fish homogenate; MA-MEDPOL 1/TM Trace elements in fish homogenate; standard 2976 Trace elements and Me-Hg in mussel tissues, etc.), blanks and analytical duplicates were used in parallel with sample measurements. Recovery of certified values ranged between 90% - 110%. Method detection limits (MDLs), limit of quantification (LOQ), and precision (e.g., relative standard deviation < 10%) were also evaluated (**Table 2**).

2.2. Evaluation of Essentiality and Toxicity of Metals

2.2.1. Nutritional Requirement Index (NRI)

NRI is commonly used to compare the metal concentration in biota to the recommended dietary intake for humans or known physiological requirements for the species. Usually is used for essential elements and not for toxic ones.

$$\text{NRI} = \frac{C_{\text{biota}} \times \text{IR}}{\text{RDI}}$$

where: C_{biota} = concentration in edible tissue (mg/kg); IR = ingestion rate (kg/day); RDI = recommended daily intake for humans (mg/day). If NRI ≈ 1: optimal intake; NRI < 1: insufficient to meet dietary needs; NRI > 1: above requirement (may be excessive if significantly high). In **Table 3** below, there are presented the RDI values for metals. According to FAO 2020/2021, the average consumption rate for Albanian people ranges between 10 - 15 kg/365 days, meaning 27 - 41 g/day. Further, we will use 40 g/day as the maximum IR.

Table 3. RDI values of studied metals.

Metal	RDI/AI (Adults)	Unit	Notes
Iron (Fe)	8 (men)/18 (women)	mg/day	Higher for women due to menstruation
Zinc (Zn)	11 (men)/8 (women)	mg/day	Important for immune and enzyme function
Copper (Cu)	0.9	mg/day	Cofactor in many enzymes
Manganese (Mn)	2.3 (men)/1.8 (women)	mg/day	AI, not RDI – limited data
Chromium (Cr)	35 (men)/25 (women)	µg/day	AI – involved in carbohydrate metabolism
Magnesium (Mg)	400 (men)/310 (women)	mg/day	Also found in fish muscle
Calcium (Ca)	1000	mg/day	Sometimes present in bones/shells of seafood

2.2.2. Risk Assessment

Non-carcinogenic health risk assessment through seafood consumption (USEPA, 2000) was based on the formula calculation as below:

$$\text{THQ} = (\text{EFr} \times \text{ED} \times \text{IR} \times \text{C})/(\text{RfD} \times \text{BW} \times \text{AT})$$

where C = metal concentration in food (mg/kg), RfD = reference dose (mg/kg/day), IR = ingestion rate (40 g/day), BW = body weight (70 kg), etc. THQ < 1 suggests no significant risk; THQ ≥ 1 suggests potential health risk [33]. Hazard Index (HI) was used to evaluate the combined non-carcinogenic risk from multiple metals. It was calculated using the below formula:

$$\mathrm{HI} = \sum \mathrm{THQ}_i$$

where THQ_i is the target hazard quotient for each individual metal. HI ≥ 1 suggests potential health risk. Calculation of HI and THQ were referred to the data given in Table 4. In this evaluation, Ca and Mg were excluded as no toxic effects are evident for respective elements.

Table 4. RfD values of metals.

Metal	RfD (mg/kg/day)	Source	Notes
Chromium	0.003	USEPA	Carcinogenic; Cr III is essential and less toxic
Copper (Cu)	0.04	USEPA	High doses can cause liver damage
Zinc (Zn)	0.3	WHO/FAO	Excess may inhibit copper and iron absorption
Iron (Fe)	0.7	WHO/FAO	RfD rarely used; toxicity mainly at high doses
Manganese (Mn)	0.14	USEPA	Neurotoxicity concern at high intake

2.2.3. Benefit-Risk Ratio (BRR)

The Benefit-Risk Ratio (BRR) is used to compare the nutritional benefit of essential elements (like selenium, iron, or zinc) to the potential health risk from toxic elements (like mercury, cadmium, or lead) in seafood or other foods. It is a useful tool in food safety, especially when the same food contains both beneficial and harmful elements.

$$\mathrm{BRR} = \frac{\mathrm{EDI}_{\text{beneficial}} / \mathrm{TNRI}_{\text{beneficial}}}{\mathrm{EDI}_{\text{tox}} / \mathrm{RfD}_{\text{tox}}}$$

where $\mathrm{EDI}_{\text{beneficial}}$ accounts for percentage of RDI for metal X at 40 g/day; Total NRI accounts for sum of NRI for Fe, Zn, Cu, Cr, Mn; Hazard Index (risk from all trace metals). A higher BRR means greater nutritional benefit relative to toxicological risk. All species here show very high BRQ (>300), indicating excellent nutritional value with minimal risk.

3. Results and Discussions

3.1. Descriptive Statistics

In this study, concentration of metals Fe, Cu, Zn, Cr, Mn, Ca and Mg was determined in 33 samples of marine biota, including tissues and organs. Table 5 presented the descriptive statistics of the obtained results, including minimum, mean, range, maximum and confidence interval values. Concentrations of essential trace elements were generally within safe intake limits: Zn (1.0 - 84 mg/kg), Cu (0.50 - 13.0 mg/kg), Fe (0.51 - 208 mg/kg), Ca (36 - 21,566 mg/kg), and Mg (20 - 1497 mg/kg).

Table 5. Descriptive statistics of metals concentration in biota samples (mg/kg ww).

Parameter	Fe	Zn	Cu	Cr	Mn	Ca	Mg
Mean	10.41	11.10	2.27	0.074	0.94	4912	245.8
Standard Error	6.24	2.73	0.43	0.006	0.17	1113	44.3
Median	2.41	5.46	1.24	0.071	0.43	1975	185.4
Standard Deviation	35.90	15.70	2.49	0.034	0.96	6391	254.3
Range	208.00	83.55	12.50	0.126	2.90	21530	1476
Minimum	0.51	1.05	0.49	0.019	0.02	36	20.7
Maximum	208.00	84.60	12.99	0.145	2.91	21566	1497
Confidence Level (95.0%)	12.72	5.57	0.88	0.012	0.34	2266	90.2
MLD (μg/l)	0.2	0.05	0.2	0.2	0.05	0.01	0.002
LOQ (μg/l)	0.56	0.14	0.56	0.56	0.14	0.028	0.006

3.2. Determination of Nutritional Requirement Index

This table presents the extended Nutritional Requirement Index (NRI) values for essential trace and macro elements in marine biota species consumed in Albania. NRI is calculated using the formula: NRI = (Concentration × Ingestion Rate/RDI) × 100 Assumed ingestion rate: 0.04 kg/day. The Total NRI is the sum of the individual contributions. In the graphs of Figure 1, the obtained results regarding the Total NRI values of respective species as well as Total NRI of each analysed metal.

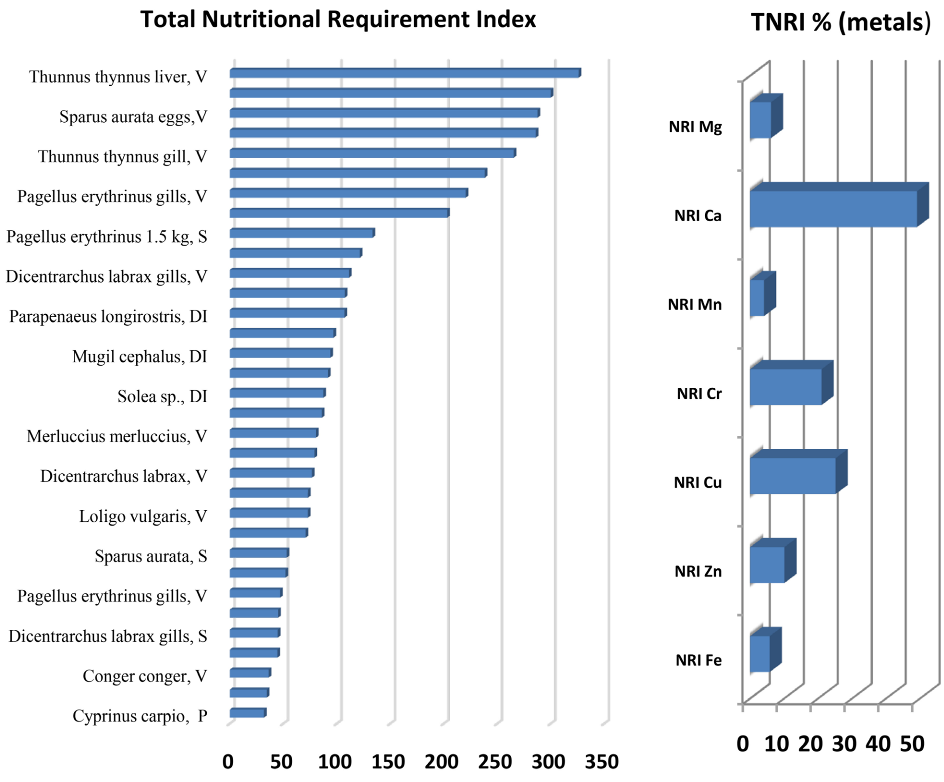


Figure 1. Total NRI of selected species (left) and metals (right).

Marine species show wide variation in NRI values, with some like *Thunnus thynnus* and *Pagellus erythrinus* gills, presenting extremely high total NRIs, indicating dense micronutrient content. Organs (e.g., liver, gills) tend to accumulate higher levels of essential elements, leading to elevated NRIs compared to muscle tissue, which typically has lower mineral content. Exceptionally Iron (Fe) was found high in *Thunnus thynnus* liver; Zinc (Zn) and Copper (Cu) notably high in *Pagellus erythrinus* liver and Calcium (Ca) was especially high in *Sparus aurata* gills and *Pagellus erythrinus* gills. While high NRIs indicate nutritional benefits, bioaccumulation in organs also raises concerns for potential metal toxicity—highlighting the need for risk assessment alongside benefit analysis.

3.3. Assessment of Benefit Risk Ratio, BRR

In the graph below there are presented results obtained for the Benefit Risk Ratio, BRR on selected species. Calculations were referred to a rate of consumption at 40 g/day. All species here showed very high BRQ (>250), indicating excellent nutritional value with minimal risk. The highest values were found in species *Dicentrachus labrax* and *Sparus aurata*, assuming for the safest species to be consumed. (**Figure 2**)

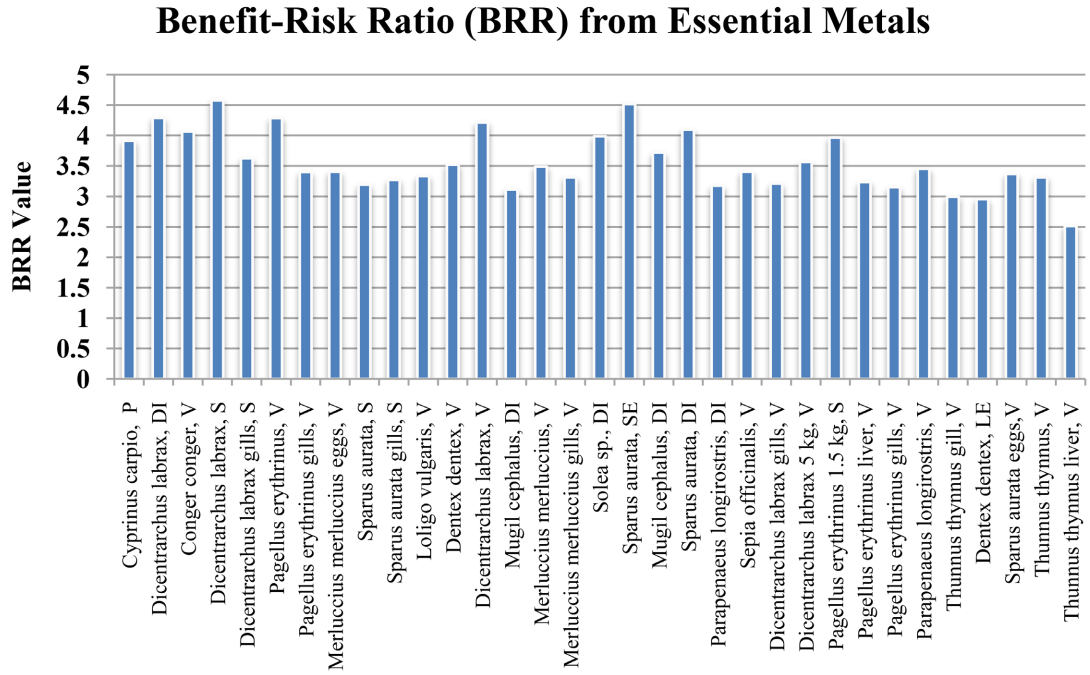
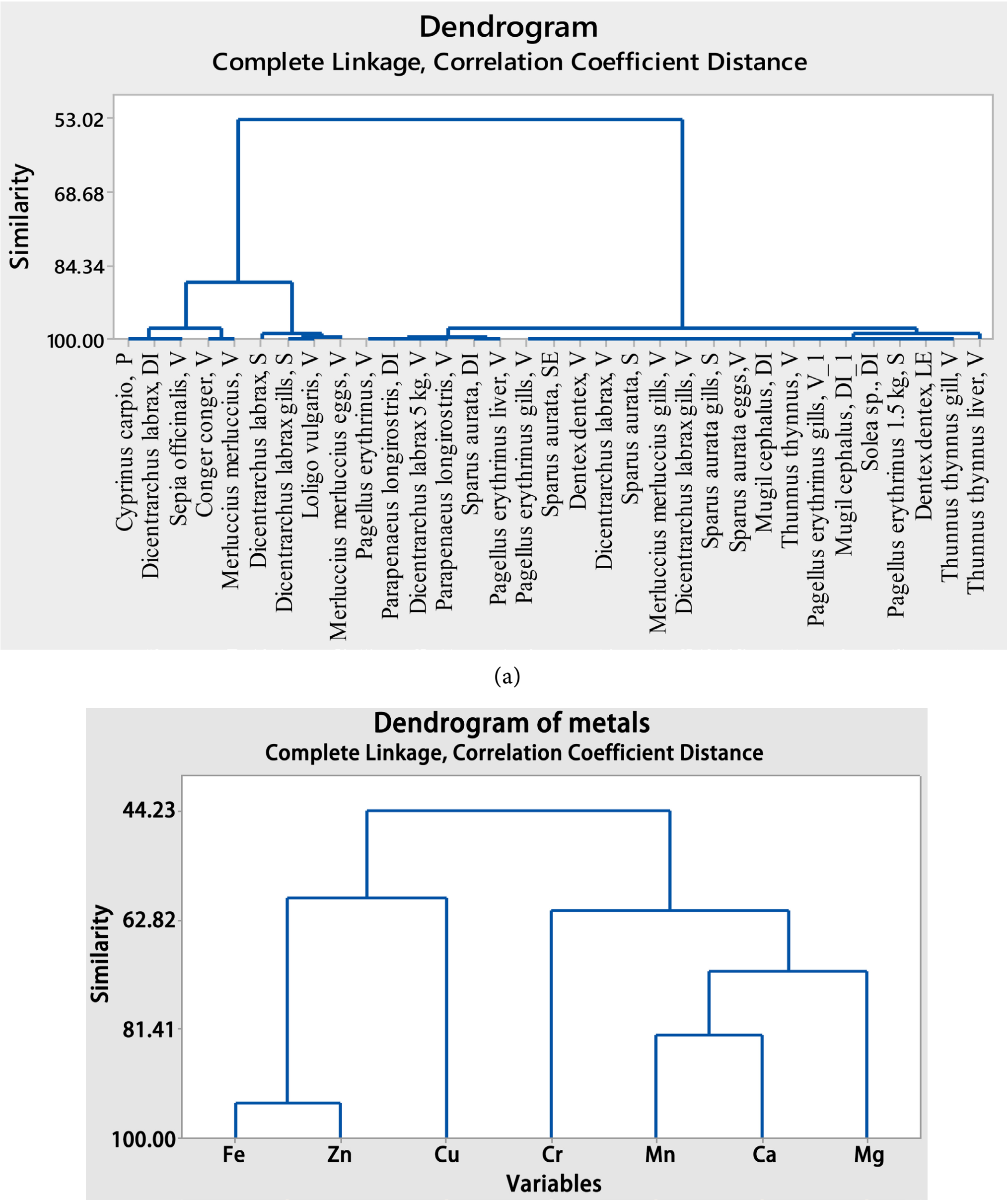


Figure 2. Benefit/Risk ratio in selected species.

3.4. Cluster Analysis

Cluster analysis was used aiming to find similarities between selected species with regard to metals concentration. Also, origin of the presence of metals in biota species was evaluated by cluster analysis of metals. Results are presented in graphs of **Figure 3**.



(a)

(b)

Figure 3. Cluster analysis of selected species (a) and metals (b).

The dendrogram of species groups together fish and other marine organisms with similar metal accumulation profiles. Obtained results indicated that species were grouped based on type of tissue; location and species and organ type. For example, gills and liver samples tend to cluster together (e.g., *Sparus aurata gills*, *Pagellus erythrinus gills*, *liver of Pagellus*) due to high concentrations of Fe and Zn, which are known to accumulate in metabolically active tissues; species from Vlore like *Conger conger*, *Merluccius*, and *Pagellus erythrinus* tend to cluster together [32], suggesting regional pollution patterns or similar ecological niches; coastal filter feeders (*Parapenaeus longirostris*, *Sepia officinalis*) form separate clusters, likely due to distinct uptake mechanisms as well as outliers:

Thunnus thynnus liver stands out with exceptionally high Fe and Zn, forming a distinct branch—indicative of bioaccumulation at higher trophic levels.

The metal dendrogram reveals how metals are grouped based on co-occurrence in marine species: Fe and Zn are closely clustered: these are essential elements, involved in oxygen transport and enzyme activity. They often co-accumulate in tissues like liver and gills; Cu and Mn form a secondary cluster: both are micronutrients and may share biological uptake pathways; Cr appears as a moderately distinct branch, likely reflects environmental rather than biological sources, especially if present in trace amounts; Ca and Mg form a distinct cluster far from trace metals: these are macro elements, absorbed in large quantities and influenced by osmo-regulation, not pollution.

4. Conclusions

The presence of trace and macro elements in marine organisms is an important indicator of both environmental health and nutritional value. This study investigated the concentration of seven key elements (Fe, Zn, Cu, Cr, Mn, Ca, Mg) in edible and non-edible tissues of marine species collected along the Albanian coast, aiming to assess their implications for human consumption and environmental quality.

Most species significantly contribute to the RDI for Fe, Zn, and Cu at a consumption rate of 40 g/day. Liver and gills offer high nutritional benefits but are not typically consumed. Ca and Mg intake from seafood alone is generally insufficient to meet daily requirements. All species here showed very high BRQ (>250), indicating excellent nutritional value with minimal risk.

EDI and THQ values for all metals were below RfD thresholds. HI values were well below 1 for all species, indicating low risk. Slightly elevated THQ values were observed for Cr and Mn in some samples.

Cluster Analysis separated tissues by metal accumulation profiles. Essential trace metals clustered together; Ca and Mg formed a distinct group. Cr was isolated, suggesting potential anthropogenic sources. Cluster analysis confirmed species grouping by tissue type and metal profile.

Marine species from the Albanian coast are generally safe for consumption regarding metal content. They provide valuable nutritional benefits, particularly for Fe, Zn, and Cu. Liver and gill tissues exhibit higher metal loads and require continued monitoring. Pollution levels are low, but special attention should be given to Cr concentration. Clustering are effective tools for monitoring and source identification.

Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

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