E-ISSN: 2347-5129
P-ISSN: 2394-0506
(ICV-Poland) Impact Value: 76.37
(GIF) Impact Factor: 0.549
IJFAS 2023; 11(6): 38-42

www.fisheriesjournal.com
Received: 12-09-2023
Accepted: 14-10-2023

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Levels of heavy metals in mussels (*Mytilus galloprovincialis* Lamark, 1819) from the black sea (Sinop, Turkey)

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DOI: https://doi.org/10.22271/fish.2023.v11.i6a.2876

Abstract
The primary objective of this study was to assess the concentrations of Cobalt (Co), Nickel (Ni), Manganese (Mn), and Iron (Fe) in the consumable parts of the Mediterranean mussel, scientifically known as *Mytilus galloprovincialis* (Lamarck, 1819). These mussels were collected from the Sinop coast, situated along the Black Sea. This species holds significance as an economic resource and an indicator organism for environmental monitoring. The edible portions of the mussel specimens were meticulously isolated, and the quantities of Cobalt (Co), Nickel (Ni), Manganese (Mn), and Iron (Fe) were quantified using Inductively Coupled Plasma Mass Spectrometry (ICP-MS). The mean concentrations of these elements in the edible tissues of the mussels were determined to be 0.68±0.01mg/kg, 2.35±0.05mg/kg, 16.81±1.44mg/kg, and 719.41±17.87mg/kg, respectively. It is noteworthy that the sequence of predominance of these metals within the mussels was as follows: Iron (Fe) exhibited the highest concentration, followed by Manganese (Mn), Nickel (Ni), and Cobalt (Co).

Keywords: Black Sea, Mussels, *Mytilus galloprovincialis*, Heavy metals, ICP-MS, Bioaccumulation

1. Introduction

Metal pollution in coastal areas is a prominent source of apprehension due to its deleterious impacts and propensity to accumulate within marine ecosystems [1, 2]. The presence of metallic pollutants in coastal ecosystems is primarily ascribed to processes such as the combustion of fossil fuels, activities within the metal industry, mining operations, and the release of municipal sewage. Additionally, the influx of freshwater can transport a substantial load of chemical contaminants downstream into the marine coastal region. A marine environment polluted with heightened levels of metals poses a potential risk to human health, as these contaminants can ultimately find their way to consumers through the food chain, as noted by Belivermiş *et al.* [3].

Mussels have been extensively utilized as a means to evaluate the concentrations of metals in open oceans, estuaries, and coastal inlets owing to their widespread geographic presence, substantial population, and their capacity to accumulate and concentrate environmental contaminants [3-12]. The Mediterranean mussel *Mytilus galloprovincialis*, holds particular promise for toxicological research. It is worth noting that the impact of heavy metal concentrations in seawater on mollusks is not solely dependent on the metal concentrations in the surrounding environment but is also influenced by the size of the mollusc [9].

Rivers constitute the primary origin of contamination in the Black Sea, with pollutants, as approximated by Zaitsev's [13] terrestrial pollution assessments, encompassing 90,000 tons of iron, 12,000 tons of zinc, 45,000 tons of lead, 80 tons of mercury, 2,800 tons of copper, and 1,500 tons of chromium being introduced annually [14]. The Bulgarian coastline plays a role in the pollution and eutrophication of the Black Sea via its seventeen rivers and three lakes. Mirinchev *et al.* [15], executed a study concentrating on the consequences of heavy metal contamination from these rivers within the region.

Jitar *et al.* [16] have denoted, "To assess the state of the Black Sea ecosystems, during the last years, many authors studied the heavy metals in the sediments, water, and organisms”.

Given the limited self-purification capability of the Black Sea, scientific investigations concerning parameters that can serve as pollution indicators are of utmost importance for acquiring reliable data and raising awareness. Consequently, this study determined the levels of cobalt (Co), nickel (Ni), manganese (Mn), and iron (Fe) in the edible tissues of the Mediterranean mussel, *Mytilus galloprovincialis*, which is ecologically and economically significant in the Black Sea coastal area.

2. Materials and Methods
2.1 Study Area
The area of study and the location where mussel specimens were collected are illustrated in Figure 1. Mussel samples were gathered in the coastal waters of Sinop (Black Sea) at depths of 0-5 meters from July to September 2022 (Figure 2, Table 1).

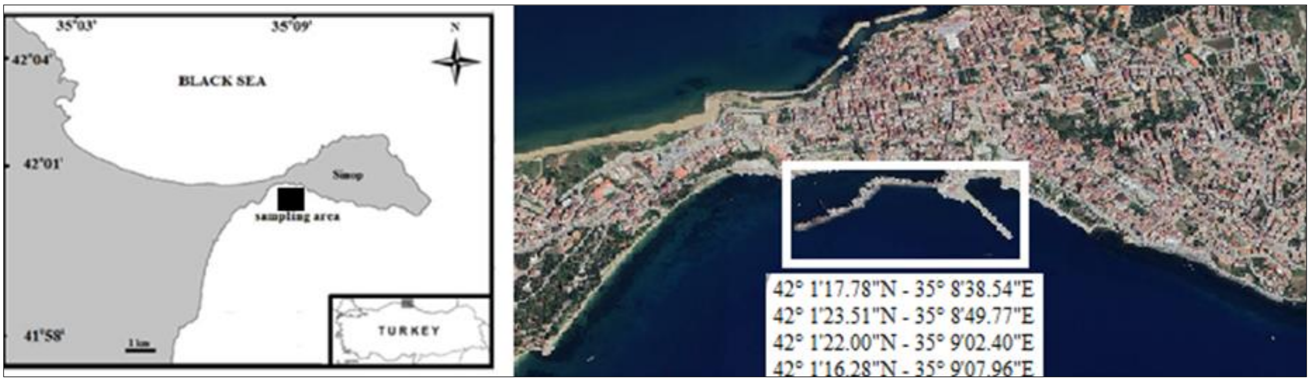

Fig 1: The map of the study area

Fig 2: Mediterranean mussel (*Mytilus galloprovincialis*)

Table 1: Total weight and information of mussels

Samples/Name	Scientific name	Number of samples	Sampling date/month	Total weight of mussels (g)		
				Min	Max	Mean ± SD
Mediterranean mussel	*Mytilus galloprovincialis*	125	2022 / July-September	13.7	30.1	22,25±0.28

2.2 Sample preparation and trace element analysis
The *Mytilus galloprovincialis* samples used in the study, with a size exceeding 6 cm, were collected from the Sinop coast, thoroughly cleaned, rinsed, and transported to the laboratory in sterile plastic bags along with seawater, where they were stored at -18 °C. The edible portions of the mussel samples were carefully separated from their bivalve structures without causing damage to the tissues for subsequent analysis.

The separated tissues were weighed, and values for Co, Ni, Mn, and Fe in all samples were determined using an ICP-MS spectrophotometer following microwave processing. Co, Ni, Mn, and Fe concentrations were analysed in triplicate, and the average of the values obtained in the study was reported.

2.3 Statistical Analysis
The findings are depicted in terms of average values and their corresponding standard errors. Statistical examinations were carried out using the SPSS 21 statistical software package. A priori significance thresholds of 0.01 and 0.05 were defined, with p-values below 0.01 and 0.05 denoting statistical significance. Additionally, the association between the levels of heavy metals in the mussel specimens was evaluated using Pearson correlation analysis.

3. Results and Discussion
The study presents the Co, Ni, Mn, and Fe values determined in mussels' consumed tissues (Figure 3).

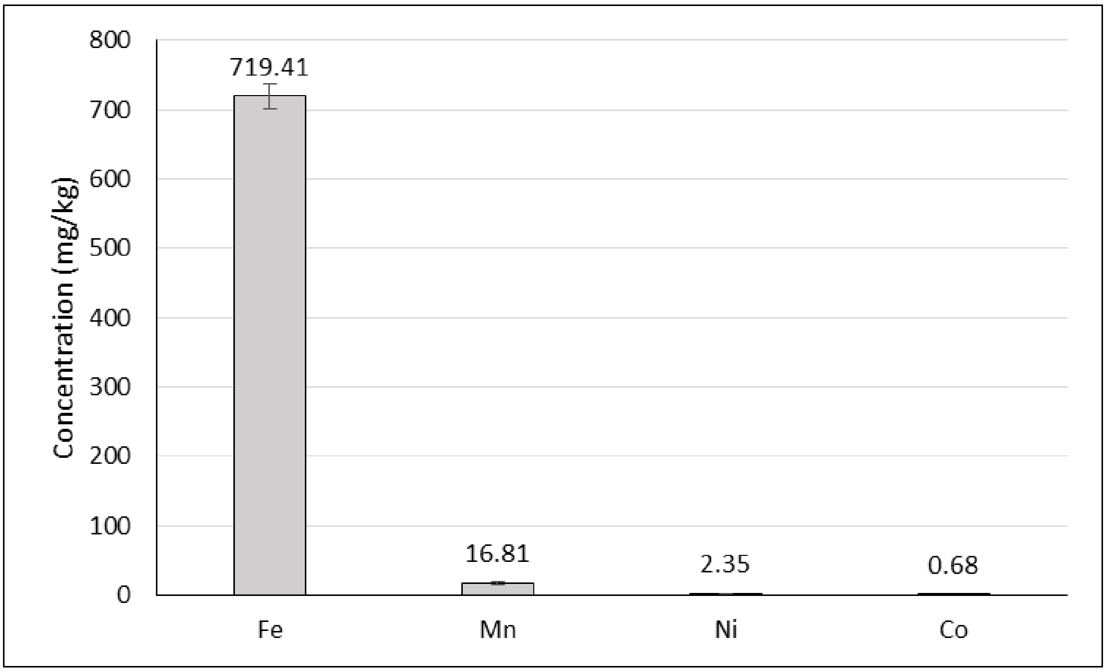

Fig 3: The bioaccumulation of metals in edible bivalve *Mytilus galloprovincialis*

The average levels of Co, Ni, Mn, and Fe in the edible tissues of mussels were determined to be 0.68±0.01mg/kg, 2.35±0.05mg/kg, 16.81±1.44mg/kg and 719.41±17.87mg/kg, respectively. According to the results, the highest concentration was observed for Fe, followed by Mn, which had the second-highest concentration among the analysed metals. Based on the findings, the metal levels were ranked as Fe>Mn>Ni>Co. The correlation coefficients of Co, Ni, Mn, and Fe elements in the soft tissues of mussels are provided in Table 3.

Table 3: Correlation analysis results of heavy metal analysis

	Co	Ni	Mn	Fe
Co	1	*	*	**
Ni	0,877	1		**
Mn	-0,902	-0,585	1	*
Fe	-0,980	-0,955	0,799	1

*Correlation is significant at the 0.05 level
** Correlation is significant at the 0.01 level

In the process of statistically evaluating the correlation coefficients and associations among constituents present in the consumable portions of mussels, it was ascertained that there was a substantial positive correlation between Mn and Fe (r=0.799), a notably strong positive correlation between Co and Ni (r=0.877), a moderate inverse correlation between Ni and Mn (r=0.585), and a remarkably strong inverse correlation among Co and Mn, Co and Fe, as well as Ni and Fe (with correlation coefficients of r=0.902, r=0.980 and r=0.955, respectively).

In the study by Topçuoğlu *et al.* [5], heavy metal concentrations in mussel samples collected in 1997 from the Sinop (Black Sea) coast were reported as follows: 1.79mg.g^{-1} dry weight for Co, 4.02 for Ni, 22.8 for Mn, and 598 for Fe.

Tepe and Süer [17] determined the average values of Fe, Ni, Co, and Mn in mussel samples collected from the Giresun (Black Sea) coast as 161.08 mg.kg^{-1} wet wt, 12.70, 1.97, and 6.23, respectively.

In their study of heavy metal content in mussel samples collected from the Sinop (Black Sea) coast, Belivermiş *et al.* [3] reported values of 0.69µgr.gr^{-1} wt for Co, 5.8 for Mn, 3.1 for Ni, and 154 for Fe.

In their study of mussel samples from Sevastopol Bay (Black Sea), Chelyadina *et al.* [12] indicated a value of 0.08 µgr.gr^{-1} for Co and 0.74µgr.gr^{-1} for Ni.

In a study on the biological accumulation of metals in edible bivalves (Saccostrea cucullate, Meretrix casta, and Villorita cyprinoides), conducted by Deep and Nasnodkar [18], it was reported that the accumulation ranking of all three species was similar to the current study, with Fe>Mn>Ni>Co.

Various inherent aspects, such as age, dimension, sexual characteristics, genetic makeup, physical characteristics, and lipid content, shape the concentration of metals within marine organisms. Additionally, external factors, such as the presence of metals in a form that living organisms can take up, proximity to the source of these metals, and the physical and chemical properties of water, including thickness, salinity, pH, redox potential, and ionic composition, play a crucial role in this process. These variables jointly regulate the retention of specific metals within the soft tissues of marine organisms, as previously discussed in works by Saavedra *et al.* [19] and Mubiana *et al.* [20].

The estimated daily intake of metals in the human body based on consumption, expressed in µg/kg/day, is specified by WHO [21] as 300 for Ni and 800 for Fe. Additionally, USEPA [22] has provided a range of 200-500 for Mn.

4. Conclusion

This study utilized Mediterranean mussels (*Mytilus galloprovincialis*) collected from the Sinop (Black Sea) coasts as bioindicator organisms due to their dietary and lifestyle characteristics. The levels of Co, Ni, Mn, and Fe in the soft tissues were determined as 0.68±0.01mg/kg, 2.35±0.05mg/kg, 16.81±1.44mg/kg, and 719.41±17.87mg/kg, respectively. According to the results, the metal levels were ranked as Fe>Mn>Ni>Co.

Cobalt (Co) is a crucial component of vitamin B12 and serves as a cofactor for numerous enzymes [23, 24]. However, this trace element can become toxic at relatively low concentrations, leading to apoptosis, necrosis, inflammation,

and genotoxic effects in mammals [25]. Nickel (Ni) is primarily discharged into aquatic environments through municipal and industrial wastewater [26]. While it plays an essential biological role in some invertebrates due to its presence in enzymes' active sites, high concentrations of Ni can be toxic and inhibit DNA repair mechanisms [27]. Manganese (Mn) is incorporated into metabolism as an enzyme cofactor, particularly in cellular respiration, and is abundant in cell mitochondria [3, 28]. Iron (Fe) is derived from various oxidized minerals abundant in the Earth's crust, such as hematite, magnetite, limonite, and siderite. Among heavy metals, iron is most commonly found in mussels and algae structures [29, 30]. Fe, Mn, Cu, and Zn are essential for marine biota's biochemical and physiological functions [31].
The Black Sea is characterized by limited natural circulation and is subject to domestic and industrial wastewater inputs along its coasts. The Black Sea coasts receive wastewater inputs from point and diffuse sources. Therefore, conducting heavy metal studies in aquatic organisms with sessile characteristics, such as mussels, in the water, sediment, and, as in this study, is essential for assessing the pollution load of the environment.

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