

EVALUATION OF POTENTIALLY TOXIC ELEMENTS IN BLACK SEA FISHERY RESOURCES: A REVIEW

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Abstract

Environmental pollution is a worldwide problem and heavy metals (HM) constitute one of the most important challenges. Due to industrialization and urbanization, Black Sea is considered as one of the most polluted seas in the world. The aim of the current study is to provide a state-of-the-art review related to the evaluation of potentially toxic elements in fishery resources from Black Sea. As a result, various data sources were revised and the appropriate information was centralized in order to acquire a clear sight on concentrations dynamics and accumulation tendency of the most hazardous HM and metalloids, as it follows: Ni, Cd, Zn, Hg, Fe, As, Cr and Pb. Accordingly, the aforementioned multitude of chemical pollutants bio-accumulates in fishery resources and are being a particular concern in relation to their harmful effects on human health.

Key words: heavy metals, fishery resources, Black Sea.

INTRODUCTION

Marine environment is constantly under increasing pressure, due to a large category of human activities, as waste water discharges and sea-based activities (shipping, mariculture, seabed mining, dredging of sediment and dumping at sea) (Tornero and Hanke, 2016).

The Black Sea is overload by excessive amounts of nutrients and hazardous substances from the anthropogenic activities and the major rivers that flow into it (Danube, Dniپر and Dniesta) (Krutov, 2019).

Its waters have been widely perceived as being heavily contaminated, although thus far there are little reliable data about the number of contaminants that are being discharged in the Black Sea, or about their concentrations in water, sediment or biota.

Pollutants like fertilizers, pesticides, pharmaceutical chemicals, microplastics, heavy metals, and petroleum hydrocarbons are harmful for the environment (Auta et al., 2016). Generally, a density of at least 5 g cm^{-3} , an atomic mass higher than 23 either an atomic number exceeding 20, are used to define a heavy metal (Koller et al., 2018). Also, heavy metals are considered if their density is five times higher comparing to water density (Simionov et al., 2019).

Literature classifies heavy metals in two categories: essential heavy metals (Cu, Mg, Zn, Fe, Se, Co) which are biodegradable and decay quickly into harmless or less harmful forms (Bat et al., 2019) and non-essential heavy metals (Cd, Pb, Al, Sb, Sn, As, Bi) that are described as potentially toxic trace elements (Simionov et al., 2019) which are non-biodegradable and remain for a long time in biota (Bat et al., 2019).

Heavy metals are regularly listed as one of the most toxic element from marine environment, due to their persistence in the ecosystem, their toxicity and bioaccumulative nature (Khan et al., 2018).

The European Union consider any chemical which have a wet mass bioconcentration factor (BCF_w) >100 , as potentially accumulator in consumers moreover is considered as being destructive for aquatic biota and food chain (Jitar et al., 2015). Marine organisms like bivalves and fish, accumulate heavy metals most often higher concentrations than sediment or water (Karsli, 2021). Even so, the heavy metals accumulation in biota is influenced by the bioavailability of the metal in the water, the type of the metal, size, sex or reproductive cycle, and also the environmental hydrodynamics (Simionov et al., 2019). Thus, heavy metals brought about through the food

chain as a consequence of pollution are potential chemical hazards and threaten consumers (Karsli, 2021).

The Black Sea fishery resources, that is shared by Romania, Georgia, Bulgaria, Russia Federation, Turkey and Ukraine, are an integral part of those societies, and make important contribution to social health and economic (Kevern and Serge, 2009).

This study provides kinds information that are available in literature and contributes to a better comparison of the potentially toxic elements from the Black Sea fishery resources.

Therefore, keeping in view of the potentially toxic elements, as well as metal concentrations in fishery resources from the Black Sea it is considered necessary to acquire a baseline environmental data, to ensure consumer protection and consequent compliance with food safety regulations.

MATERIALS AND METHODS

This study systematically reviews a multitude of studies on potentially toxic elements in the Black Sea fishery resources. Eight heavy metals including Pb, As, Cd, Cr and Hg were comprehended in this study, all of which are priority pollutants, designated by The Food and Agricultural Organisation (FAO) of the United Nations. A total of 89 indexed publications were gathered, but it was required to narrow the searching area, in order to achieve an appropriate number of articles for review. From the main literature databases in addition to Science Direct, Research Gate, Web of Science, Google Scholar, PubMed and international standards from FAO, this review gather only papers that presented results about heavy metal concentrations from fishery resources. Using a mixture of searching methods (electronic and manual), this review collected data about heavy metal concentration of 73 samplings sites from the Black Sea. Each of these findings just studied a single species or a few species, across different points from the Black Sea. The data used in the centralised table (Table 1) includes concentration values retrieved from the scientific literature published

in the timeline 2010 to 2022 (older scientific paper were considered to be obsolete). Therefore, the aim of the present study was to assess the potentially toxic elements in the Black Sea fishery and associated risks of heavy metals, identified in recent past. The metal concentrations of fishery resources from the Black Sea have been widely reported in the recent literature. This review provides a national scale assessment through bringing together all the data of these literatures.

RESULTS AND DISCUSSIONS

With the increased use of the Black Sea fishery resources, is essential to frequently update the inventory of the types and also the quantities of potentially toxic elements released in the sea. Along these lines, is essential to find out the relative influence of all human activities and how they interact to the impact of marine ecosystems.

This review, present in an easy way, an appraisal of a few heavy metals like: Ni, Cd, Zn, Hg, Fe, As, Cr and Pb, their concentrations from: *Engraulis encrasicolus*, *Merlangius merlangus*, *Trachurus trachurus*, *Sarda sarda*, *Mullus barbatus*, *Mugil cephalus*, *Psetta maxima*, *Pomatomus saltatrix*, *Sprattus sprattus*, *Mytilus galoprovincialis* and *Rapana venosa* as well as possible effects on humans after consuming of them.

The statistics of the concentrations of heavy metals detected in the Black Sea fishery resources of this review are given in Table 1.

Methods to measure and assess the effects of heavy metals concentrations in aquatic ecosystems are very complex by factors that are both: external and internal to the organism, along with the interrelatedness of the toxic elements themselves (Burger, 2007).

Individual organisms and species are affected differently depending on their breeding cycle, foraging methods, and geographical ranges.

The Black Sea is a semi-closed sea, and is having shared stocks, moreover all the countries that share the Black Sea, are required to manage fishery resources with common measures.

Table 1. Data regarding heavy metals concentrations in different fish species according to different authors

Fishery resources	Reference	Heavy Metals								Area	
		Ni	Cd	Zn	Hg	Fe	As	Cr	Pb		
<i>Engraulis encrasicolus</i>	Nisbet et al. (2010)	3.12*	0.035*	26.25*	-	26.06*	-	-	-	0.7*	Turkish coast of the Middle Black Sea
	Aygun and Abanoz (2011)	-	0.2*	175.15*	-	34*	-	-	-	0.4*	Samsun coasts in Middle Black Sea
	Görür et al. (2012)	0.01*	-	15.05*	-	13.41*	2.08*	0.1*	0.02*	0.02*	Middle Black Sea (Turkey)
	Alkan et al. (2013)	0.48*	0.3*	8.22*	-	-	1.85*	0.73*	0.03*	0.03*	Southeastern area of the Black Sea
	Bat et al. (2014)	-	-	9.05**	-	-	0.61**	-	-	-	Sinop (Turkey)
	Bat et al. (2014)	-	-	11.3**	-	-	0.66**	-	-	-	Samsun (Turkey)
	Bat et al. (2014)	-	-	12.2**	-	-	0.54**	-	-	-	Fatsa (Turkey)
	Bat et al. (2014)	-	-	12.35**	-	-	0.605*	-	-	-	Batumi (Georgia)
<i>Merlangius merlangus</i>	Gundogdu et al. (2016)	0.69*	0.47*	38.39*	-	20.59*	-	-	-	0.905*	Coast of Sinop in the Middle Black Sea (Turkey)
	Alkan et al. (2016)	0.48*	0.3*	-	-	-	1.85*	-	-	-	Southeastern area of the Black Sea.
	Plavan et al. (2017)	0.234**	0.0435**	-	-	-	-	0.017*	-	-	Romanian territorial area of the Black Sea
	Baltas et al. (2017)	4.16*	0.003*	2.32*	-	227.2*	-	-	-	0.02*	Rize Harbor (Turkey)
	Karsli (2021)	0.0055**	0.0135**	20.55**	0.02**	9.605**	1.285*	0.03**	0.02**	0.02**	Black Sea coasts of Turkey, Georgia, and Abkhazia
	Nisbet et al. (2010)	-	0.002*	31.34*	-	11.59*	-	-	-	0.58*	Turkish coast of the Middle Black Sea
<i>Merlangius merlangus</i>	Mendil et al. (2010)	-	0.18*	20.6*	-	27.7*	-	0.82*	0.46*	0.46*	Turkish coast
	Aygun and Abanoz (2011)	-	0.2*	58*	-	9.9*	-	-	-	0.9*	Samsun coasts in Middle Black Sea
	Görür et al. (2012)	0.03*	-	0.51*	-	16.06*	1.32*	0.16*	0.01*	0.01*	Middle Black Sea (Turkey)
	Bat et al. (2015)	-	0.02**	3.4**	0.05**	0.87**	1.24**	-	-	0.05**	Sinop Coastal Waters (Turkey)
	Alkan et al. (2016)	0.61*	0.031*	21.5*	-	-	6.34*	0.62*	0.024*	0.024*	Samsun coasts in Middle Black Sea (Turkey)

Fishery resources	Reference	Heavy Metals										Area
		Ni	Cd	Zn	Hg	Fe	As	Cr	Pb			
<i>Trachurus trachurus</i>	Nisbet et al. (2010)	-	0.012	27.7	-	21.17	-	-	-	0.6	Turkish coast of the Middle Black Sea	
	Mendil et al. (2010)	-	0.22	25.7	-	36.4	-	0.95	0.64	Turkish coast		
	Alkan et al. (2013)	0.53	0.27	18.12	-	-	2.58	0.74	0.03	Southeastern area of the Black Sea.		
	Makedonski et al. (2015)	0.008	0.008	0.6	0.16	-	0.73	-	0.06	Coastal waters of Bulgarian Black Sea		
	Gundogdu et al. (2016)	0.49	0.07	23.685	-	25.47	-	-	0.55	Sinop in the Middle Black Sea (Turkey)		
<i>Sarda sarda</i>	Plavan et al. (2017)	0.32	0.0163	-	-	-	-	0.013	0.102	Romanian territorial area of the Black Sea		
	Nisbet et al. (2010)	3.04	0.025	19.55	-	25.96	-	-	0.9	Turkish coast of the Middle Black Sea		
	Mendil et al. (2010)	-	0.35	21	-	25.5	-	0.64	0.28	Turkish coast		
	Bat et al. (2012)	-	0.025	15.155	-	-	-	-	0.16	Sinop Coastal Waters (Turkey)		
<i>Mullus barbatus</i>	Makedonski et al. (2015)	0.11	0.015	0.13	0.13	-	0.41	-	0.06	Coastal waters of Bulgarian Black Sea		
	Nisbet et al. (2010)	2.47	0.02	23.71	-	29.17	-	-	0.92	Turkish coast of the Middle Black Sea		
	Mendil et al. (2010)	-	0.23	17.8	-	41.4	-	0.99	0.4	Turkish coast		
	Jitar et al. (2014)	0.27	0.02	-	-	-	-	0.02	0.32	Romanian coastline of Black Sea		
	Bat et al. (2015)	-	0.02	3.2	0.05	2.3	1.3	-	0.05	Sinop Coastal Waters (Turkey)		
	Alkan et al. (2016)	0.46	0.018	19.7*	-	-	14.75	0.56	0.02	Samsun coasts in Black Sea (Turkey)		
<i>Mugil cephalus</i>	Gundogdu et al. (2016)	0.47	0.11	15.085	-	16.84	-	-	0.28	Sinop in the Middle Black Sea (Turkey)		
	Bat et al. (2012)	-	0.025	36.765	-	-	-	-	0.14	Sinop Coastal Waters (Turkey)		
	Stancheva et al. (2013)	-	0.024	-	0.08	-	0.9	-	0.07	Bulgarian Black Sea coast		
	Engin et al. (2015)	0.044	-	13.545	-	1.157	2.011	4.806	-	Bulancak (Turkey)		
	Engin et al. (2015)	0.063	-	13.07	-	2.692	2.42	9.073	-	Giresun port (Turkey)		
	Engin et al. (2015)	0.699	-	6.726	-	1.067	0.928	0.165	-	Waste area of Giresun (Turkey)		
	Engin et al. (2015)	0.042	-	10.609	-	0.752	1.573	3.966	-	Unye (Turkey)		
	Engin et al. (2015)	0.47	-	4.279	-	1.007	0.855	0.147	0.03	Samsun port (Turkey)		
	Makedonski et al. (2015)	0.009	0.012	5.2	0.05	-	1.1	-	0.05	Coastal waters of Bulgarian Black Sea		

Fishery resources	Reference	Heavy Metals										Area
		Ni	Cd	Zn	Hg	Fe	As	Cr	Pb			
<i>Psetta maxima</i>	Nisbet et al. (2010)	3.22*	0.022*	24.83*	-	21.72*	-	-	-	-	-	Turkish coast of the Middle Black Sea
	Simionov et al. (2019) ²	0.105*	0.3*	12.18*	-	9.13*	3.81*	-	-	-	-	Romanian coastline of the Black Sea
<i>Pomatomus saltatrix</i>	Nisbet et al. (2010)	1.91*	0.025*	25.51*	-	23.81*	-	-	-	-	-	Turkish coast of the Middle Black Sea
	Makedonski et al. (2015)	0.009**	0.008**	10**	0.09**	-	0.77*	-	-	-	-	Coastal waters of Bulgarian Black Sea
<i>Sprattus sprattus</i>	Bat et al (2012)	-	0.07**	41.845*	-	-	-	-	-	-	0.26**	Sinop Coastal Waters (Turkey)
	Alkan et al. (2013)	0.3*	0.25*	0.87*	-	-	2.58*	-	-	-	0.01*	Southeastern area of the Black Sea
<i>Mytilus galoprovincialis</i>	Jitar et al. (2014)	0.25*	0.06*	-	-	-	-	0.05*	-	-	0.07*	Romanian coastline of Black Sea
	Makedonski et al. (2015)	0.028**	0.005**	0.05**	0.12**	-	0.73*	-	-	-	0.08**	Coastal waters of Bulgarian Black Sea
<i>Mytilus galoprovincialis</i>	Plavan et al. (2017)	0.158**	0.018**	-	-	-	-	-	0.019**	-	-	Romanian territorial area of the Black Sea
	Jitar et al. (2014)	1.05*	0.22*	-	-	-	-	-	0.89*	-	1.36*	Romanian coastline of Black Sea
<i>Rapana venosa</i>	Rosioru et al. (2016)	8.62*	1.95*	-	-	-	-	-	4.56*	-	0.11*	Romanian coastline of Black Sea
	Tepe and Sürer (2015)	12.7*	-	69.06*	-	161.1*	3.16*	-	0.56*	-	31.6*	Giresun coasts of the Black Sea (Turkey)
<i>Rapana venosa</i>	Strungaru et al. (2017)	0.53**	0.193**	-	-	-	-	-	1.52*	-	0.088*	Romanian-Ukraine border of the Black Sea
	Jitar et al. (2014)	0.52*	1.1*	-	-	-	-	-	0.88*	-	1.29*	Romanian coastline of Black Sea
<i>Rapana venosa</i>	Mülayim and Balks (2015)	-	0.85*	-	1.1*	-	-	-	0.15*	-	0.4*	Thrace Coast of the Black Sea (Turkey)
	Strungaru et al (2017)	0.156**	-	-	-	-	-	-	0.03*	-	0.012*	Romanian-Ukraine border of the Black Sea

- not measured; * based on dry weight; ** based on wet weight.

The Black Sea is a semi-closed sea, and is having shared stocks, moreover all the countries that share the Black Sea, are required to manage fishery resources with common measures. Some targeted species, such as shellfish, may be relatively stable and thus considered fully resident in national waters for management purposes. The major capture fisheries in the Black Sea, on the other hand, migrate within the Black Sea and are shared with other Black Sea stakeholders. In the near future, international agreements and national initiatives may compel countries to develop common fisheries management plans. As a result, every country should be prepared for such actions.

Nickel concentration in various fishery resources from the Black Sea area

Nickel is an important nutrient for organisms, although at high concentrations, it can be toxic. (Rosioru et al., 2011). The toxicity of nickel-containing substances, like that of other metals, is thought to be related to the bioavailability of the metal ion (Ni^{2+}) at systemic or local target sites. (Goodman et al., 2011). Considering there are no bioavailability normalization approaches for Ni in marine systems, all of the data presented here are expressed as dissolved concentrations.

The maximum permissible limit value of Ni, accepted by FDA is 80 $\mu\text{g/g}$ and the WHO (World Health Organization, 1992) recommends 100-300 μg Ni for daily intake for human adults.

The highest concentration of Ni was found in *Mytillus galoprovincialis* (12.7 $\mu\text{g/g}$ in wet weight) in Giresun coasts of the Black Sea (Turkey coastline) and the lowest concentration was registered in *Trachurus trachurus* (0.008 $\mu\text{g/g}$ in wet weight) in coastal waters of Bulgarian Black Sea (Figure1).

Nickel allergic contact dermatitis, respiratory carcinogenicity, reproductive toxicity, and non-cancer respiratory effects are the main human health effects of concern associated with Ni exposure. As a result, the European Union's (EU) nickel restriction (REACH, Annex XVII, Entry 27) is based on nickel release rather than nickel content. (Buxton et al., 2019)

The consequence and effects of nickel in the environment are well known; however, metals

rarely occur singly in the aquatic environment, but rather in mixtures with other metals and toxic elements. When heavy metals develop together, they can interact with one another or with other receptors (for example, DOC), potentially affecting the bioavailability and toxicity within each individual component (Buxton et al., 2019).

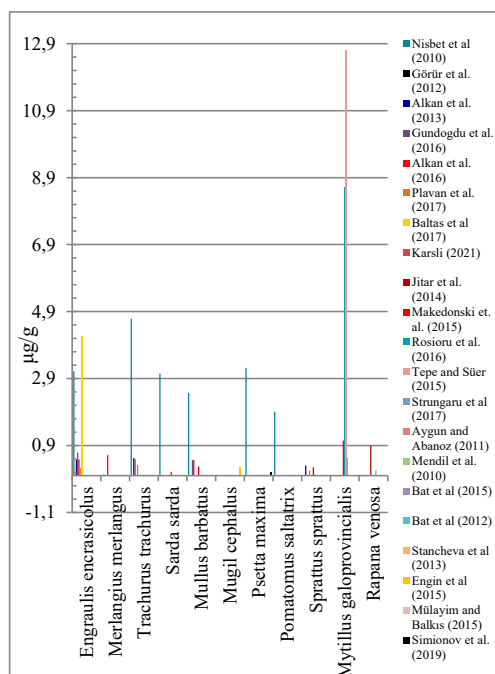


Figure 1. The Ni concentration in different fish species in the Black Sea area according to different authors

Cadmium concentration in various fishery resources from the Black Sea area

Cadmium (Cd) is a toxic heavy metal which has had serious health consequences on organisms. It is a natural element in the earth's crust and is usually found as a mineral with several other elements. Cd can be found through all type of soils and rocks, as well as coal and mineral fertilizer, likewise is commonly found in the aquatic environments at low levels and is not an essential element for animals and humans (Bat and Arici, 2018).

The Joint FAO/WHO Expert Committee on Food Additives mentioned a PTWI (Provisional Tolerable Weekly Intake) for Cd, of 0.007 $\mu\text{g/g}$ /body weight/week, and 0.025 $\mu\text{g/g}$ /body weight/month (FAO/WHO, 2010, 2011) The

EU Maximum Residue Limit (MRL) legally concentration permitted in fish is 0.1-0.3 $\mu\text{g/g}$ (Bat and Arici, 2018) additionally, the Turkish Food Codex settled the maximal level at 0.10 $\mu\text{g/g}$ for sea fish (Turkish Food Codex, 2008).

The highest concentration of Cd was registered also (as the concentration of Ni and Pb) in *Mytillus galoprovincialis* (1.95 $\mu\text{g/g}$ dry weight) in Romanian coastline of Black Sea and the lowest concentration was found in *Merlangius merlangus* (0.002 $\mu\text{g/g}$ in dry weight), in Turkish coast of the Middle Black Sea (Figure 2).

According to research, increasing salinity tends to increase Cd absorption by aquatic macrophytes, and increasing salinity leading to the formation of cadmium chloride, which cannot be absorbed by plants. If the salinity concentration rises further, the Cd in the chlorides suspended in the water will be replaced by Na, resulting in an increase in Cd concentration (Simionov et al., 2019).

Chronic exposure to high levels of cadmium can result in liver damage, bone degeneration, blood damage, and renal dysfunction. There are ample confirmations in humans for the cancer-causing nature that results from the presence of both Cd and Cd compound. (Vardhan et al., 2019)

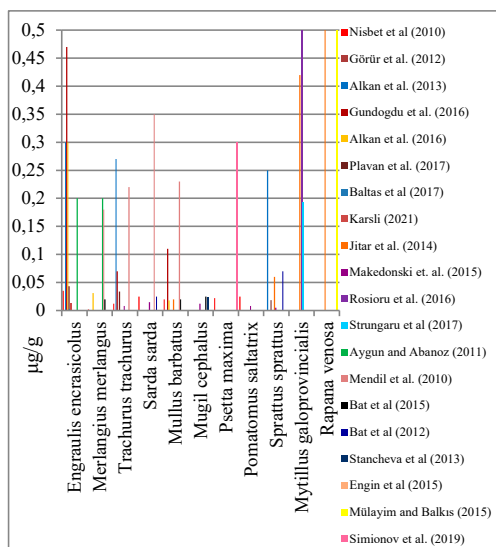


Figure 2. The Cd concentration in different fish species in the Black Sea area according to different authors

Zinc concentration in various fishery resources from the Black Sea area

Zinc (Zn) is a rare element in nature, but it has a long history of use due to its availability in limited deposits and ease of extraction from ores. It is an essential element and is available in multitudinal minerals, including ZnS, ZnO, ZnCO_3 , Zn_2SiO_4 (Vardhan et al., 2019).

The Turkish Food Codex set down the maximum Zn level tolerated of 50 $\mu\text{g/g}$ for fish (Turkish Food Codex, 2008), although the Joint FAO/WHO established the Zn provisional tolerable weekly intake (PTWI) for 7 $\mu\text{g/g}$ body weight (World Health Organization, 2007). The highest concentration of Zn (Figure 3) was registered in *Engraulis encrasicolus* (175.15 $\mu\text{g/g}$ in dry weight), in Samsun area, Turkish Black Sea coast. Meanwhile, *Engraulis encrasicolus* and *Mytillus galoprovincialis* (with a concentration of Zn- 69.06 $\mu\text{g/g}$ in dry weight), were the only reported Zn concentration which exceeds the maximum limit established by Turkish Food Codex (Turkish Food Codex, 2008).

Vomiting, dehydration, drowsiness, abdominal pain, nausea, lack of muscular coordination, and renal failure are all symptoms of acute Zn toxicity in humans. A chronic dose of Zn increase the risk of developing anemia, pancreas damage. Workers who have been exposed to Zn fumes from smelting or welding have developed a short-term illness known as mental fume fever (Sharma et al., 2005).

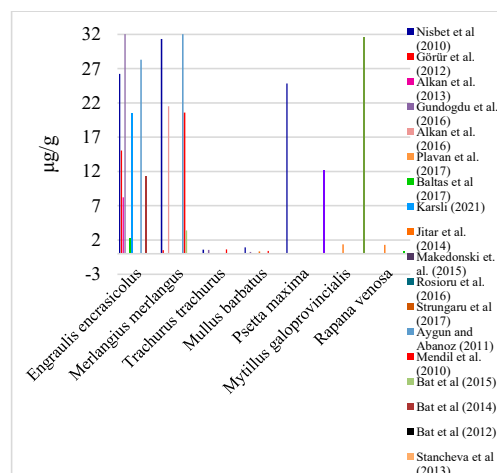


Figure 3. The Zn concentration in different fish species in the Black Sea area according to different authors

Mercury concentration in various fishery resources from the Black Sea area

Mercury is the most toxic non-essential metal for organisms. In the environment, Hg exists in three forms: elemental Hg, organic Hg as well as inorganic Hg (Jaishankar et al., 2014).

Except for *Mullus* species and *Sarda sarda*, which have a maximum permitted level of 1.0 µg/g wet weight, European legislation established a maximum level of admitted Hg concentration in fish muscle tissue of 0.5 µg/g wet weight (EC, 2006). For human adults, WHO established a provisional tolerable weekly intake (PTWI) of 0.0016 µg/g body weight (World Health Organization, 2007).

Hg concentrations were found to be highest in *Rapana venosa* (1.1 µg/g in dry weight), found in Thrace Coast of the Black Sea (Turkey), Figure 4. *Rapana venosa* is a macrobenthic organism, used commonly as biomonitor of heavy metal pollution. (Bat and Öztekin, 2016). Human exposure to high levels of Hg can cause pulmonary edema, pneumonia, and a variety of other symptoms of lung damage. In human adults, low-level Hg exposure causes depression, tremors, skin rashes, memory loss, and peeling off hands and feet, as well as redness (Sharma and Agrawal, 2005).

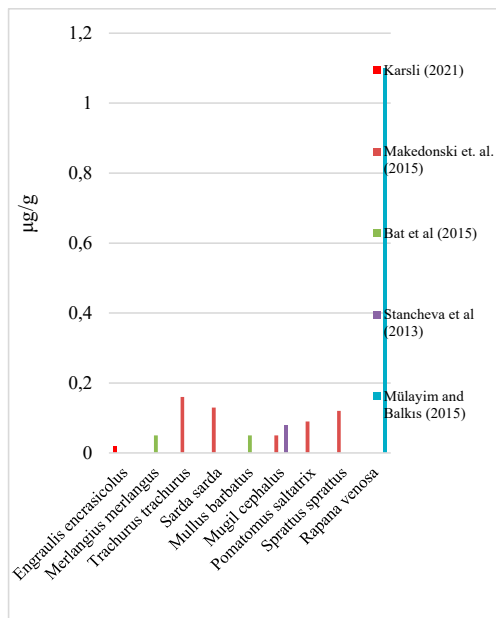


Figure 4. The Hg concentration in different fish species in the Black Sea area according to different authors

As concentration in various fishery resources from the Black Sea area

Arsenic (As) is a common environmental pollutant, and human exposure occurs through contaminated water and soil, as well as through arsenic-rich food (e.g., garlic, marine food). (Florea and Büsselberg, 2006).

Human health concerns about the high levels of arsenic found in some seafood have increased interest in marine ecosystems. For example, Alkan et al., (2016) found the highest concentrations of As from all the papers that were reviewed (14.75 µg/g in dry weight) in *Mullus barbatus*, in Samsun coasts in Middle Black Sea (Turkey). Therefore, the lowest concentration of As was registered in *Sarda sarda* (0.41 µg/g in wet weight), in coastal waters of Bulgarian Black Sea (Figure 5). According to Makedonski et al. (2015), the concentrations of As that he found in his study, was generally low in all the species, compared to data in the literature and world food standards.

Arsenic in its inorganic form is a known carcinogen. Low to moderate amounts of As exposure lead to diabetes, renal and hepatic dysfunction, also neurological problems. Women are more prone to As induced skin diseases than males because their skin is more vulnerable to As and causes dermatitis (Sharma and Agrawal, 2005).

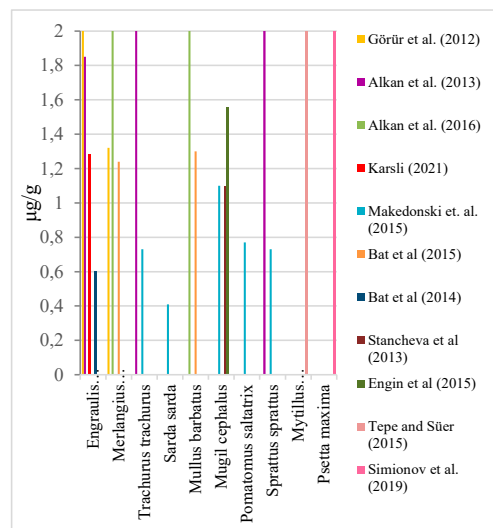


Figure 5. The As concentration in different fish species in the Black Sea area according to different authors

Iron concentration in various fishery resources from the Black Sea area

Iron (Fe) is an essential element, necessary for life, also an important component of many proteins and many enzymes, including many that participate in the generation of high energy metabolites.

In case of Fe (Figure 6), the highest concentration was registered in *Engraulis encrasicolus* (227.2 µg/g in wet weight) in Rize Harbor (Turkey), followed by *Mytilus galoprovincialis* (161.08 µg/g in wet weight) in Giresun (Turkish coast). Though the Joint FAO/WHO established the limit of the maximum permissible amount of Fe at 425.5 µg/g.

According to Simionov (2019), essential metals, such as Fe, accumulate at a higher concentration than non-essential metals, which can be explained by their role in metabolism function. In the case of fish, the existing mechanism for metal uptake from the environment implies the interaction of proteins and amino acids. Consumption of ascorbic acid-containing foods may increase Fe availability (Stancheva et al., 2010).

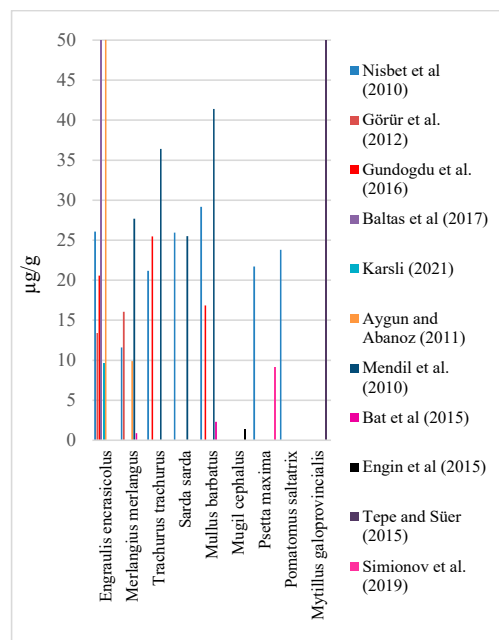


Figure 6. The Fe concentration in different fish species in the Black Sea area according to different authors

Cr concentration in various fishery resources from the Black Sea area

Elemental chromium (0) did not actually exist in nature. Trivalent chromium (III) is a trace metal that is required for the forming of glucose tolerance factor as well as the metabolism of insulin. (Barceloux, 1999) and can have a toxic effect when is present in very large quantities (Baruthio, 1992).

According to the EFSA, (European Food Safety Authority, 2014) the maximum Cr level permitted is established at 0.3 mg/kg. The highest concentration of Cr was registered in *Mugil cephalus* (9.073 µg/g in dry weight) in Giresun port of Turkey (Figure 7). The lowest concentration was recorded in *Mullus barbatus* (0.002 µg/g in dry weight), in Romanian coastline of the Black Sea. Cr participate in lipid metabolism and insulin function (Simionov et al., 2019).

The most significant hazardous effects of hexavalent chromium compounds after contact, inhalation, or ingestion: Dermatitis, allergic and eczematous skin reactions, ulcerations of the skin and mucous membranes, perforation of the nasal septum, allergic asthmatic reactions, bronchial carcinomas, gastro-enteritis (Baruthio, 1992).

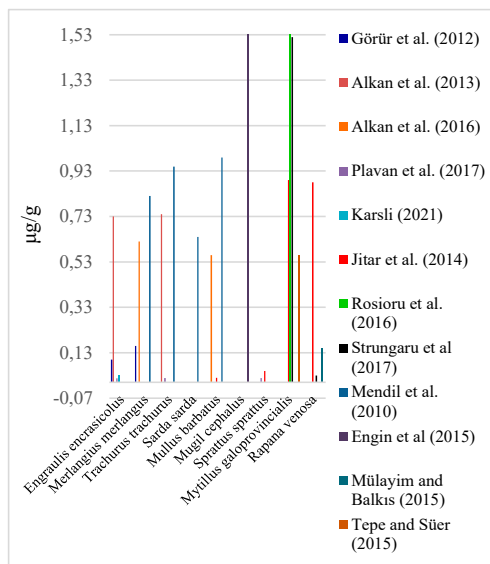


Figure 7. The Cr concentration in different fish species in the Black Sea area according to different authors

Lead concentration in various fishery resources from the Black Sea area

Lead (Pb) is considered as a toxic heavy metal, although it was widely used for more than 5000 years because this metal is corrosion resistant, dense, ductile and malleable. Therefore it was deployed for building materials, pigments to glaze ceramics, ammunition, ceramics glazers, glass and crystals, paints, protective coatings, acid storage batteries, gasoline additives, cosmetics. Due to its wide use, humans are exposed to lead derivatives and have a daily intake by food, drinking water and by inhalation (Florea and Büsselberg, 2006).

The European legislation (EC, 2006) dispose the maximum level of Pb permitted in the muscle tissue of fish of 0.30 mg/kg wet weight, also, the Joint FAO/WHO suggest a provisional tolerable weekly intake (PTWI) of 0.025 mg/kg body weight, for human adults (World Health Organization, 2007). The highest Pb concentration was found in *Mytilus galloprovincialis* (31.6 µg/g in wet weight), in the Giresun coasts of the Black Sea (Turkey) (Figure 8). It is the only reported Pb concentration that exceeds the established maximum limit.

Pb has serious effects on the body even at low concentrations. Pb interferes with a variety of processes, including protein folding, inter- and intracellular signaling, enzyme regulation, and cell adhesion, apoptosis. Hypertension is caused by a high level of Pb exposure.

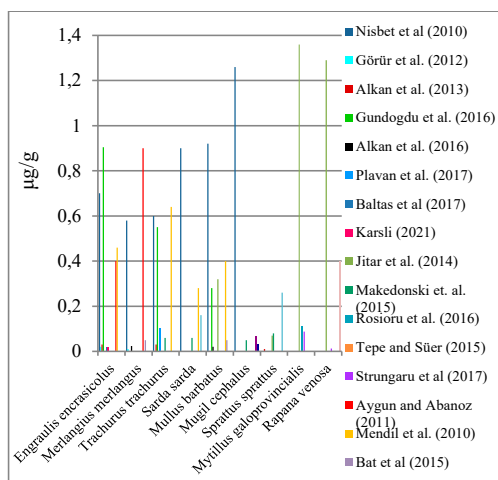


Figure 8. The Pb concentration in different fish species in the Black Sea area according to different authors

CONCLUSIONS

The outcome of the present study identified that consuming fish and molluscs from Romania, Ukraine, Bulgaria, Turkey and Georgia, may not have a harmful impact on human health. Nonetheless an increase in the number of fish and seafood servings consumed per week may cause mercury, lead and arsenic-related health problems for consumers across the board. The growing global population is causing people to seek out new foods in order to obtain adequate and balanced nutrition. Seafood is one of the most important foods consumed to meet peoples protein requirements. They do, however, play an important role in the transmission of various pollutants, including heavy metals, to humans. As a result, determining toxic substance levels in edible parts of fishery resources on a regular basis is critical for both, food and environmental safety. Clearly, this is not intended to be a complete and definitive list of potentially toxic elements in Black Sea fishery resources, but rather a consolidated starting point for acknowledging chemical pollution from coastal to open sea environments.

The mean concentrations of the investigated heavy metals were found to be the highest for Zn (175.15 µg/g), followed by Pb (31.6 µg/g), and the lowest for Fe (227.2 µg/g), followed by Ni (12.7 µg/g). Comparing the average values recommended of heavy metals with European Food Safety Authority, World Health Organization, European legislation, and Turkish Food Codex, it was found that Zn, Cd, Hg, Cr, and Pb exceeded the highest permitted values.

As a result, the Black Sea receives a large amount of pollution from multiple sources. This demonstrates the importance of pollution control not only from the six Black Sea riparian countries, but also from all of the countries within the Black Sea basin. In this regard, every country in the basin bears some responsibility for the Black Sea pollution. As a result, coordinated and collaborative efforts are required. Commitment fulfillment and adherence to Strategic Action Plan recommendations are critical to achieving the goals of reduced pollution and improved water quality.

Another conclusion to be drawn from the current review is that the metal concentrations of fishery resources from the Black Sea have been barely reported in the recently literature, thus is a lack of information about the real status of HM pollution in the Black Sea region. In order to stop and prevent pollution in the Black Sea, countries in the Black Sea Basin, must implement additional deterrent legislation. Furthermore, continuous pollution measuring stations in the Black Sea must be established at specific points to monitor pollution and create an inventory. Hence, the Black Sea pollution sources are numerous, and the effects on aquatic organisms should be determined periodically.

REFERENCES

- Alkan N, Alkan A, Gedik K, Fisher A. (2013). Assessment of metal concentrations in commercially important fish species in Black Sea. *Toxicol Ind Health*. 32(3), 447-56.
- Alkan, A., Alkan, N., Akbaş, U. (2016). The factors affecting heavy metal levels in the muscle tissues of whiting (*Merlangius merlangus*) and red mullet (*Mullus barbatus*). *Tarım Bilimleri Dergisi*. 22. 349-359
- Auta, H.S., Emenike, C.U., Fauziah, S.H. (2017). Distribution and importance of microplastics in the marine environment: a review of the sources, fate, effects, and potential solutions. *Environ. Int*. 102, 165-176
- Aygun, S., and Abanoz, F. (2011). Determination of Heavy Metal in Anchovy (*Engraulis encrasicolus* L 1758) and Whiting (*Merlangius merlangus euxinus* Nordman, 1840) Fish in The Middle Black Sea. *Kafkas Üniversitesi Veteriner Fakültesi Dergisi*. 17. S145-S152.
- Baltas H, Kiris E, Sirin M. (2017). Determination of radioactivity levels and heavy metal concentrations in seawater, sediment and anchovy (*Engraulis encrasicolus*) from the Black Sea in Rize, Turkey. *Mar Pollut Bull*. 116(1-2), 528-533
- Barceloux D.G. (1999). Chromium. *Journal Toxicol Clin Toxicol*. 37(2)
- Baruthio F. (1992). Toxic effects of chromium and its compounds. *Biol Trace Elem Res*. 32:145-53
- Bat, L., Murat, S., Üstün, F., Sahin, F. (2012). Heavy Metal Concentrations in Ten Species of Fishes Caught in Sinop Coastal Waters of the Black Sea, Turkey. *Turkish Journal of Fisheries and Aquatic Sciences*. 12. 371-376.
- Bat, L., & Yalçın, K., Öztekin, H.C. (2014). Heavy Metal Levels in the Black Sea Anchovy (*Engraulis encrasicolus*) as Biomonitor and Potential Risk of Human Health. *Turkish Journal of Fisheries and Aquatic Sciences*. 14. 845-851.
- Bat, L. Öztekin, H., Üstün, F.. (2015). Heavy Metal Levels in Four Commercial Fishes Caught in Sinop Coasts of the Black Sea, Turkey. *Turkish Journal of Fisheries and Aquatic Sciences*. 15. 399-405.
- Bat, L., Öztekin, H.C. (2016). Heavy metals in *mytilus galloprovincialis*, *Rapana venosa* and *Eriphia verrucosa* from the Black Sea coasts of turkey as bioindicators of pollution. 13. 715-728.
- Bat, L. and Arici, E. (2018). Heavy Metal Levels in Fish, Molluscs, and Crustacea From Turkish Seas and Potential Risk of Human Health in Handbook of Food Bioengineering. *Academic Press*, 5, 159-19
- Bat, L., Arıcı, E., Öztekin, A. (2019). Heavy metals health risk appraisal in benthic fish species of the Black Sea. *Indian Journal of Geo-Marine Sciences*. 48. 163-168.
- Brewer, G.J (2010). Risks of Copper and Iron Toxicity during aging in humans. *Chemical Research in Toxicology*
- Burger J. (2007). A framework and methods for incorporating gender-related issues in wildlife risk assessment: gender-related differences in metal levels and other contaminants as a case study. *Environ Res*. 104(1).
- Buxton, S., Garman, E., Heim, K.E., Lyons-Darden, T., Schlekot, C.E., Taylor, M.D., Oller, A.R. (2019). Concise Review of Nickel Human Health Toxicology and Ecotoxicology. *Inorganics*. 7(7):89
- Directive, (2006), Directive 2006/1881/EC the Commission of the European Communities Setting maximum levels for certain contaminants in foodstuffs (Text with EEA relevance), Official Journal of the European Union, L 364/5, 20.12.2006
- EFSA (European Food Safety Authority), (2014) Scientific Opinion on the risks to public health related to the presence of chromium in food and drinking water. *EFSA J*, 12, 3595.
- Engin, M.S., Uyanik, A., Cay, S., Kir, I. (2016). Evaluation of trace metals in sediment, water, and fish (*Mugil cephalus*) of the central Black Sea coast of Turkey, Human and Ecological Risk Assessment: An International Journal, 22:1, 241-250
- FDA (U.S. Food and drug administration), (2007). Action Levels, Tolerances and Guidance Levels for Poisonous or Deleterious Substances in Seafood, Section IV, Chapter II.04. National Shellfish Sanitation Program Guide for the Control of Molluscan Shellfish. USA: FDA.
- Florea, A.M., Büsselberg, D. (2006). Occurrence, use and potential toxic effects of metals and metal compounds. *Biometals*, 19, 419-427.
- Food and Agricultural Organization of the United Nations and World Health Organization, (2011), Joint FAO/WHO Expert Committee on Food Additives Summary and Conclusions, Issued 4, JECFA/74/SC.
- Goodman, J.E., Prueitt, R.L., Thakali, S., Oller, A.R. (2011). The nickel ion bioavailability model of the carcinogenic potential of nickel-containing substances in the lung. *Crit Rev Toxicol*. 41(2)
- Görür, F.K., Keser, R., Akçay, N., Dizman, S. (2012). Radioactivity and heavy metal concentrations of

- some commercial fish species consumed in the Black Sea Region of Turkey, *Chemosphere*, 87 (4), 356-361.
- Gundogdu, A., Culha, S.T., Kocbas, F., Culha, M. (2016). Heavy metal accumulation in muscles and total bodies of *Mullus barbatus*, *Trachurus trachurus* and *Engraulis encrasicolus* captured from the coast of Sinop, Black Sea, *Pakistan Journal of Zoology*, 48 (1), 25-34.
- Jaishankar, M., Tseten, T., Anbalagan, N., Mathew, B. B., Beeregowda, K. N. (2014). Toxicity, mechanism and health effects of some heavy metals. *Interdisciplinary toxicology*, 7(2), 60–72.
- Jitar, O., Teodosiu, O., Oros, A., Plavan, G., Nicoara, M. (2015). Bioaccumulation of heavy metals in marine organisms from the Romanian sector of the Black Sea, *New Biotechnology*, 32 (3), 369-378.
- Karsli, B. (2021). Determination of metal content in anchovy (*Engraulis encrasicolus*) from Turkey, Georgia and Abkhazia coasts of the Black Sea: Evaluation of potential risks associated with human consumption. *Mar Pollut Bull.* 165:112108.
- Kevern, L.C. & Serge, M.G. (2009). A fishery manager's guidebook- second edition. *The Food and Agriculture Organization of the United Nations and Wiley-Blackwell*.
- Khan, S, Cao, Q, Zheng, Y.M, Huang, Y.Z, Zhu, Y.G. (2008). Health risks of heavy metals in contaminated soils and food crops irrigated with wastewater in Beijing, China. *Environmental Pollution*, 152.
- Koller, M., & Saleh, H.M. (2018). Introductory Chapter: Introducing Heavy Metals. In H.E M. Saleh, & R.F. Aglan (Eds.), *Heavy Metals. IntechOpen*.
- Krutov A. (2019). State of the Environment of the Black Sea (2009-2014/5). *Publications of the Commission on the Protection of the Black Sea Against Pollution (BSC) 2019*, Istanbul, Turkey, 811 pp. Retrieved February 15, 2022, from (<http://www.blacksea-commission.org/Inf.%20and%20Resources/Publications/SOE2014/>)
- Makedonski, L., Peycheva, K., Stancheva, M. (2015). Determination of some heavy metal of selected black sea fish species. *Food Control*. 72.
- Mee, L.D. (1992). The Black Sea in crisis: a need for concerted international action. *Ambio* 21, 278–286.
- Mendil, D., Zafer Demirci, Z., Tuzen, M., Soylak, M. (2010). Seasonal investigation of trace element contents in commercially valuable fish species from the Black sea, Turkey, *Food and Chemical Toxicology*, 48 (3).
- Mülayim, A. Balkis, H. (2015). Toxic metal (Pb, Cd, Cr, and Hg) levels in *Rapana venosa* (Valenciennes, 1846), *Eriphia verrucosa* (Forsk., 1775), and sediment samples from the Black Sea littoral (Thrace, Turkey), *Marine Pollution Bulletin*, 95 (1), 215-222
- Nisbet, C., Terzi, G., Pilgir, O., Sarac, N. (2010). Determination of Heavy Metal Levels in Fish Samples Collected from the Middle Black Sea. *Kafkas Üniversitesi Veteriner Fakültesi Dergisi*. 16. 119-125.
- Plavan, G., Jitar, O., Teodosiu, C., Nicoara, M., Micu, D., Strungaru, S.A. (2017). Toxic metals in tissues of fishes from the Black Sea and associated human health risk exposure. *Environ Sci Pollut Red* 24, 7776-7787
- Rosioru, D.M, Oros, A., Lazar, L. (2016). Assessment of the heavy metals contamination in bivalve *mytilus galloprovincialis* using accumulation factors. 17. 874-884.
- Sharma, R.K, and Agrawal, M. (2005). Biological effects of heavy metals: an overview. *J Environ Biol*. 26.
- Simionov, I.A, Cristea, V., Petrea, M.P, Sirbu, E.B (2019). Evaluation of heavy metals concentration dynamics in fish from the black sea coastal area: an overview. *Environmental Engineering and Management Journal*, 18 (5), 1097-1110.
- Simionov, I.A, Cristea, V., Petrea, M, Mogodan Antache, A., Nicoara, M., Baltag, E., & Strungaru, S.A., Faggio, C. (2019). Bioconcentration of Essential and Nonessential Elements in Black Sea Turbot (*Psetta Maxima Maeotica* Linnaeus, 1758) in Relation to Fish Gender. *Journal of Marine Science and Engineering*. 12. 1-18.
- Stancheva, M., Makedonski, L., Eliitsa, P.P. (2013). Determination of heavy metals (Pb, Cd, As and Hg) in Black Sea grey mullet (*Mugil cephalus*). *Bulgarian Journal of Agricultural Science*. 19. 30-34.
- Strungaru, S.A., Nicoara, M., Teodosiu, C., Micu, D., Plavan, G. (2017). Toxic metals biomonitoring based on prey-predator interactions and environmental forensics techniques: A study at the Romanian-Ukraine cross border of the Black Sea, *Marine Pollution Bulletin*, 124 (1), 321-330.
- Tepe, Y., Süer, N. (2016). The levels of heavy metals in the Mediterranean mussel (*Mytilus Galloprovincialis* Lamarck, 1819); Example of Giresun coasts of the Black Sea, Turkey. *Indian Journal of Geo-Marine Science (IJMS)*. 45. 283-289.
- Tornero V., Hanke G., (2016). Chemical contaminants entering the marine environment from sea-based sources: A review with a focus on European seas, *Marine Pollution Bulletin*, 112 (1-2), 17-38.
- Turkish Food Codex, (2008). Notification about determination of the maximum levels for certain contaminants in food stuff of Turkish Food Codex *Official Gazette of Republic of Turkey*
- Vardhan, K.H, Kumar, P.S. Panda, R.C (2019). A review on heavy metal pollution, toxicity and remedial measures: Current trends and future perspectives, *Journal of Molecular Liquids*, 290.
- World Health Organization, (1992), International programme on chemical safety, *Environmental Health Criteria*, 134.
- World Health Organization, (2007). Exposure of children to chemical hazards in food. *European Environment and Health Information System*, Fact Sheet No. 4.4.