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HEAVY METALS ACCUMULATION IN BLACK SEA ECOSYSTEMS: FISH SPECIES

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ABSTRACT

The purpose of the current review survey was to analyze data on the accumulation of various heavy metals in the Black Sea. Subject of study were Pb, Cd, As, Hg, Mn, Ni, Cu, Zn, Fe etc. and their content in selected commercially significant Black Sea fish species. Available data from the different Black Sea areas were presented. The extent to which established concentrations could affect human health was discussed. Health risk assessment parameters were summarized.

Key words: heavy metals, Black sea, fish, health risk.

Introduction

The Black Sea is a semi-enclosed sea with 40o27'N-46o32'N latitude and 27o27'E – 41o42'E longitude and is connected to the World Ocean through the Strait of Bosphorus. The Black Sea is surrounded by six countries located in Europe and Asia: Bulgaria, Georgia, Romania, Russia, Turkey and Ukraine. It contains the world's largest anoxic water mass (Bakan and Büyükgüngör, 2000; Altas and Büyükgüngör, 2007).

It receives freshwater inputs from some of the largest rivers in Europe. The three main rivers, part of the Black Sea Basin are Danube (801 463 km2), Dnieper (504 000 km2) and Don (422 000 km2) (Drainage Basin Of The Black Sea). Anthropogenic activities such as mining, industry and agriculture lead to elevation of metal concentrations in aquatic environment over the last few decades, which result in adverse effects not only to aquatic animals but also human being via food chain (Boran and Altnok, (2010). Furthermore shipping and inflow of untreated waters from coastal cities contribute to adverse environmental situation in the sea. For this reason, Black Sea is considered one of the most polluted in the world. The fishery yield has declined dramatically, and the tourism industry in the region of Bulgarian coast also suffers from serious pollution of the Black Sea.

Accumulation of trace elements depends on numerious abiotic and biotic factors. Among the first one are abiotic like the distribution of metals in an environment, salinity, temperature, and pH of the water; the type of habitat (Jakimska et al., 2011). Important biotic factors are body size and mass, age, phenotypic differences, sex, physiological conditions, developmental stage, metabolism, availability of food (Canli and Atli, 2003). Spatial and inter-annual variations of trace metals in marine organisms lead to the need for periodic and multidimensional monitoring in order to identify elevated concentrations presenting a possible health risk (Fattorini et al., 2008).

The bioaccumulation of metals in animals from different levels of the trophic pyramid represents a serious health hazard factor. Main way of exposure to a given animal appears to be the diet. The biggest problem is the concentration of metals in the tissues of animals from the upper levels of the trophic pyramid (Jakimska et al., 2011). Carnivorous species bioaccumulate greater quantities of metals than herbivores or omnivores. The main threats to human health from heavy metals are associated with exposure to lead, cadmium, mercury and arsenic (Jarup, 2003; Tchounwou et al., 2012).

The aim of the current review study was to present data, available from the last decades, for heavy metals accumulation in selected fish species from various Black sea areas.

Heavy metals accumulation in some Black sea commercially important fish species

Over the past few decades, the Black Sea ecosystem registered major changes caused either by land-based pollution or anthropogenic factors. Major fish species have declined so drastically, that they have lost their importance for commercial fishing (Radu et al., 2011).

The decrease of marine resources in the Black Sea can be explained with the following factors (Tuncer et al., 1998; Radu et al., 2011; Akkoyunlu, 2018):

– *Eutrophication* – enrichment of water by nutrient salts that causes structural changes to the ecosystem such as mass development of phytoplankton; increased mortality of demersal species; disturbance of fish behaviour, etc.;

– *Harmful substances* – oil products, radionuclides, heavy metals, pesticides, untreated waste water discharges, which affect the quality of living resources and maricultures, lead to loss of habitats and affect the quality of demersal resources by organic deposition;

– *Hydraulic works* – loss of spawning habitats of anadromous species by damming of rivers; loss of valuable habitats for spawning and feeding habitats of fish due to transforming of lagoons/limans in freshwater reservoirs; affecting the shelf habitats important for spawning and feeding of living resources through siltation from building of port dams or civil coastal defence works; changing of fish behaviour in coastal areas due to the modification of water currents by the building of big ports;

– *Alien species* – outbreak of alien species (i.e. *Mnemiopsis leidyi)* multiplied the ecological disturbance, especially at the food chain level of living marine resources and in the fish behaviour;

– *Climatic changes* – modification of river flow regimes amplifies the effect of extreme phenomena (rain, flooding etc.), especially in the marine areas under direct influence of large rivers by sharp decreasing of salinity, transparency and by replacing with freshwater species;

– *Commercial fisheries* – using non-selective fishing gears allowing the catch of non-target species and/or having undersize length; using destructive harvest techniques (dragging, bottom trawling etc.); increasing catches and fishing effort which permits stocks exploitation outside safe biological limits; illegal fishing amplifies the effect of overfishing.

According to the Executive Agency for Fisheries and Aquaculture (EAFA), the average annual quantity of consumed fish per person in Bulgaria was 5.1 kg. The most consumed marine fish species in the country according EAFA for 2013 were: mackerel (*Scomber scombrus)* – 62,4%, European sprat (*Sprattus sprattus*)- 14,8%, horse mackerel (*Trachurus mediterraneus ponticus*) – 5,1% and bluefish (*Pomatomus saltatrix*) – 0,8%.

The concentration of some heavy metals (Cd, Mn, Fe, Cu and Pb) were determined by Stancheva et al. (2010) in muscle tissue of bluefish (*Pomatomus saltatrix*) collected from Bulgarian Black Sea coast. Pb and Cd were under the detection limits and the others were in the following concentrations (mg/kg w.w): Cu – 1.34-1.46, Mn – 0.03-0.14, Fe – 6.51-7.06. The conclusions of the authors were that from an ecotoxicological point of view, the concentrations of heavy metals reflect a comparatively clean and pollution-free environment.

Gray mullet (*Mugil cephalus*) is commercially important fish species in Black Sea. Stancheva et al. (2013a) compared the Pb, Cd, As and Hg accumulation in edible part and gills of fish samples from Varna Lake and Nessebar and reported higher concentration in gills than in meat for all elements except As which was at the same time with highest concentration from all tested elements (1.10 mg/kg^{-1} w.w.). The more increased concentration in the north (Varna Lake) could be explained with the vicinity to the big Varna harbor and industries in the area.

The aim of the Makedonski et al. (2015) was to determine the levels of Cd, As, Hg, Pb, Zn and Cu in edible part and gill of seven most consumed Bulgarian fish species collected from Balchik (northern part) and Nessebar (southern part) coast of Black Sea. These fish species were sprat (*Sprattus sprattus sulinus*), Mediterranean horse mackerel (*Trachurus mediterraneus ponticus*), Black sea gobies *(Neogobius melanostromus*), shad (*Alosa pontica*), Atlantic bonito (*Sarda sarda*), bluefish (*Pomatomus saltatrix*) and grey mullet (Mugil cephalus). The fish samples were collected during 2010 and established highest element levels in the gill for all fish species. The maximum metal concentration was measured for Cu (1.40 mg/kg^{-1} w.w), Zn (11 mg/kg^{-1} w.w) and Pb (0.08 mg/kg^{-1} w.w) in muscle tissues of shad and sprat. The edible part of horse mackerel had the maximum value for Hg (0.12 mg/kg^{-1} w.w) while Atlantic bonito predominantly accumulated As (1.10 mg/kg^{-1} w.w). Among the seven metals, Zn showed the highest level of accumulation (32 mg/kg^{-1} w.w.) None the less this value was in the range according to legislation documents.

The muscle concentration of Pb, Cd, Ni and Zn of some important fish species – mackerel (*Scomber scombrus*); European sprat (*Sprattus sprattus*); horse mackerel (*Trachurus mediterraneus ponticus*) and bluefish (*Pommatomus saltatrix*) from the fish market of Varna was evaluated. The corresponding results of the above mentioned metals were as following (in μg/g): Horse mackerel – 0.166, 0.045, 0.223, 20.46; Mackerel – 0.172, 0.051, 0.142, 17.30; sprat – 0.206, 0.053, 0.205, 26.19 and bluefish – 0.194, 0.044, 0.176, 17.63 (Stoyanova et al., 2015). The reported results are clear indication of the considerable variations among the fish species in Bulgarian north Black Sea coast. The highest concentration of metals in the muscles of the studied fish species were determinate for Zn, and the lowest for Cd. The highest levels of Pb, Cd and Zh were found in sprat and the content of Ni was found to be highest of horse mackerel. The concentration of heavy metal in studied fish muscles were in the below the regulatory requirements.

Determination of As, Cd, and Pb were carried out in sprat (*Sprattus sprattus*) and goby (*Neogobius melanostomus*) from Varna. For both species, the metal concentrations increase in the order: Cd < Pb < Hg < As. The As concentration showed higher value for sprat (0.73 mg.kg^{-1}), which was significantly less than recommended from Bulgarian Food Regulation maximum levels permitted for As in sea fish (5.00 mg.kg^{-1}). The other elements were with low concentration (Stancheva et al., 2013b).

A complex heavy metal pollution study of muscle tissue of five commercially important fish species – bluefish (*Pomatomus saltatrix*), gray mullet (*Mugil cephalus*), Mediterranean horse mackerel (*Trachurus mediterraneus ponticus*), shad (*Alosa pontica*) and sprat (*Sprattus sprattus sulinus*) was conducted by Stancheva et al. (2014). The specimens were collected from Varna and Bourgas – the biggest harbors on Bulgarian coast and at the same time important industrial areas. Among the ten metals under study, iron and zinc showed the highest level of accumulation. The levels of arsenic in gray mullet were higher than the other fish species but in within the recommended legal limits. The conclusion was that the received heavy metals concentrations do not posed a risk to the fish consumers.

Another study investigated that the highest concentration of the metals Cu and Zn were found in *Trachurus mediterrneus* (0.42 mg/kg w.w) and in *Sprattus sprattus* (12.7 mg/kg w.w), respectively while the heavy metals As and Hg were found with maximum values in *Pseta maxima* (3.99 mg/kg w.w and 0.08 mg/kg w.w respectively). (Peycheva et al., 2017b).

A number of 13 elements (Ca, Mg, Na, K, Fe, Zn, Mn, Cu, Ni, Cr, As, Pb and Cd) were measured in various sample types: muscle, stomach, stomach content, intestine, intestine content, gonads, liver, spleen, gills and caudal fin of Turbot (*Psetta Maxima Maeotica*) from Constanta region of Romanian Black Sea coast. The area is considered under high anthropogenic pressure. The results represented the age, gender and organ significance for heavy metal accumulation. The gender influenced the bioaccumulation process of all analyzed elements in most tissues since turbot male specimens accumulated higher concentration of metals compared to females. The highest bioaccumulation capacity in terms of Ca, Mg, Na, Ni, As, Zn and Cd was registered in caudal fin, liver and intestine tissues. Also, other elements such as K, Fe, Cu and Mn had the highest bioaccumulation in their muscle, spleen, liver and gills tissues. The metal with highest concentration in muscle tissue was Zn – 14.06 $\mu g/g^{-1}$ w.w and with the lowest – Cd 0.03 $\mu g/g^{-1}$. The concentrations of toxic metals in Black Sea turbot from this study were lower in the muscle samples compared to the studies conducted in Turkey, suggesting that the anthropogenic activity in the studied area did not pose a major impact on the habitat contamination (Simionov et al., 2019).

The south Black Sea coast is under intensive research interest. Most of the available results originated from Sinop area (central part of Turkish Black Sea coast). Heavy metal concentrations (Zn, Co, Cd and Pb) have been measured in dorsal muscle tissue of ten species (*Trachurus mediterraneus*, *Sprattus sprattus sprattus*, *Mullus surmelatus*, *Sarda sarda*, *Mugil cephalus*, *Scorpaena porcus*, *Sparus aurata*, *Umbrina cirrosa*, *Spicara maena* and *Solea solea*) from Sinop coast of the Black Sea, Turkey. The metal content decreased in the order Zn>Cu>Pb>Cd. Zinc was with highest concentration in all species in the ranges of 5.95-45.35 mg/kg, the last of which was detected in sprat. (Bat et al., 2012).

Eight elements (Al, As, Cu, Zn, Hg, Fe, Cd and Pb) were explored in the muscle tissue of Red mullet (*Mullus barbatus*), Whiting (*Merlangius merlangus*), Mediterranean horse mackerel (*Trachurus mediterraneus*) and Golden grey mullet (*Liza aurata*) caught from Sinop coast. The levels of Al, Hg, Cd, Pb and Cu in all fish species except *T. mediterraneus* for Cu were below the limit of detection. Mean Cu level in Mediterranean horse mackerel was 0.67 mg/kg ww. Highest value of Zn (24.7 mg/kg wet wt) was also found in the *T. mediterraneus* which were about 7-8.5 times more than the other species. *L. aurata* have the highest Fe value (3.2 mg/kg wet wt), but have the lowest As value (0.25 mg/kg wet wt.) compared with the other fish species. The levels of As for *M. barbatus* were high (1.3 mg/kg wet wt.) and followed by *M. merlangus* (1.24 mg/kg wet wt). The concentrations of the studied heavy metals were far below the established values by the Commission Regulation (EC) (Bat et al., 2015).

The metal content in five Black Sea fish species – *Scophthalmus maximus, Spicara maena, Chelidonichthys lucerna, Alosa fallax* and *Scorpaena porcus,* caught in 2013 in the same area was in order of Fe > Zn > Cu > Al > As > Pb > Cd > Hg. All elements were below the legislation concentration limits. Still Total hazard quotient was most significant for As and Hg (Bat et al., 2017a).

Evaluation of the metals content in edible part of sprat (*Sprattus sprattus*) caught at Sinop and Samsun coasts of the Black Sea during fishing season in 2013 and 2014 showed that Al, Hg, Cd and

Pb were all below the limits of detection and Fe, Zn, Cu, As were in level far below the established toxic levels (Bat et al., 2017b).

In another economically important fish- *Sarda sarda,* from the same area of the southern Black Sea coast tested for Fe, Ni, Zn, Cu, Cd, Pb, Cr, Mn, Co, Al and Hg elements showed no Cd, Pb, Al and Hg and the concentrations of the others were considerably lower than the maximum levels set by international standards (Bat and Arici, 2016).

The research of Bat et al. (2018) was performed to detect the heavy metal amounts (Hg, As, Cd, Pb, Cu, Zn) in one of the most common fish species (*Scorpaena porcus*), captured from the Sinop coast. Maximum values of the metals were in the order: Zn>Cu>As>Pb>Hg>Cd. All studied metals in Scorpion fish were quite low and did not exceed the allowable limit.

Another complex ecotoxicological survey from Sinop coasts included seven commercial fish species (Twaite shad *Alosa fallax nilotica*, European Anchovy *Engraulis encrasicolus*, Whiting *Merlangius merlangus euxinus*, Bluefish *Pomatomus saltator*, Atlantic Horse Mackerel *Trachurus trachurus*, Red Mullet *Mullus barbatus* and Turbot *Scophthalmus maximus*). The contents of six of the main elements – Cr, Fe, Cu, Zn, Cd and Pb in the muscle tissue, were investigated. In all of the tested species Fe, followed by Zn was with highest concentration. Minimum was the content of Cd. The maximum values of Fe, Cu and Zn were recorded in *E. encrasicolus*, while the maximum values of Cr, Cd and Pb were recorded in *S. maximus*, *T. trachurus* and *M. barbatus*, respectively. The minimum values of Cr and Fe were recorded in *M. barbatus*, Cu and Cd in *S. maximus*, Zn and Pb in *M.m. euxinus* and *P. saltator*, respectively (Ergönül and Altindağ, 2014).

Study of heavy metal levels (Cr, Mn, Co, Ni, Cu, Zn, As, Cd, Pb) in the muscle tissues of Whiting (*Merlangius merlangus*) and Red Mullet (*Mullus barbatus*) from Samsun area concluded that consumption of those fish species does not pose a risk to human health (Alkan et al., 2016). In the muscle tissues, the mean concentrations of the heavy metals were determined as Zn>As>Cu>Mn>Cr>Ni>Cd>Co>Pb for whiting and Zn>As>Cu>Mn>Cr>Ni>Co>Pb>Cd for red mullet. The differences in the mean concentrations of metals (Zn: 21.5 mg/kg^{-1}, As: 6.34 mg/kg^{-1}, Co: 0.03 $mg/kg^{-1}$and Cd: 0.031 mg/kg^{-1}) for whiting and red mullet tissues (Zn: 19.7 mg/kg^{-1}, As: 14.7 mg/kg^{-1}, Co: 0.11 $mg/kg^{-1}$and Cd: 0.018 mg/kg^{-1}) were statistically significant.

A two years 2009-2010) monitoring survey of heavy metals concentration in anchovy (*Engraulis encrasicolus*) and whiting (*Merlangius merlangus euxinus*) was aimed by Aygun and Abanoz (2011). Metal concentration of anchovy have been found 34.0 μg/g for Fe; 2.0 μg/g for Mn; 129.3 μg/g for Zn; 3.7 μg/g for Cu; 0.4 μg/g for Pb; 0.2 μg/g for Cd in 2009 and of whiting have been found 9.9 μg/g for Fe; 4.3 μg/g for Mn; 58.0 μg/g for Zn; 2.3 μg/g for Cu; 0.9 μg/g for Pb; 0.2 μg/g for Cd. In 2010 metal concentration of anchovy have been found 51.5 μg/g for Fe; 4.2 μg/g for Mn; 221.0 μg/g for Zn; 3.8 μg/g for Cu in 2010, metal concentration of whiting have been found 7.0±4.6 μg/g for Fe; 3.0±0.0 μg/g for Mn; 28.3±1.0 μg/g for Zn; 2.7±0.7 μg/g for Cu. zinc and copper are understood to be higher than values in literature.

Pleuronectiformes species *Scophthalmus maximus* (Linnaeus, 1758) belonging to Scophthalmidae family, *Arnoglossus laterna* (Walbaum, 1792) belonging to Bothidae family and *Pegusa lascaris* (Risso, 1810) belonging to Soleidae family were collected from Sinop coasts of the Black Sea and were researched for heavy metals (Hg, Cd, Pb, Cu and Zn) content in edible tissues. Overall Zn was detected in higher concentrations in all species followed by Cu, Pb, Hg and Cd. The limit values given by the international organizations did not exceed in the muscle tissues of turbot, Mediterranean scald fish and sand sole. Maximum levels of the metals except Hg were found in turbot. However, the high amounts of Cd, Pb, Cu and Zn in turbot were 0.011, 0.07, 1.32 and 14 $\mu g/g^{-1}$ wet wt., respectively. The highest Hg (0.021±0.007 $\mu g/g^{-1}$ wet wt.) was found in sand sole (Bat et al., 2019).

Although heavy metals content was usually lower than the legal limits, Uluozlu et al. (2007) reported that levels of lead and cadmium in fish samples from Black Sea were higher than the recommended legal limits for human consumption. Trace metal content in fish samples were 0.73–1.83 μg/g for copper, 0.45-0.90 μg/g for cadmium, 0.33-0.93 μg/g for lead, 35.4-106 μg/g for zinc, 1.28-7.40 μg/g for manganese, 68.6-163 μg/g for iron, 0.95-1.98 μg/g for chromium, and 1.92–5.68 μg/g for nickel.

Another study which objectives were the amounts of Cd, Hg, Pb, Cu, and Zn found in the whiting (*Merlangius merlangus*.) and the red mullet (*Mullus barbatus*) mean values of Cd, Hg, Pb, Cu, and Zn in the edible tissues were 0.013, 0.024, 0.07, 0.195, and 9.05 mg/kg wet wt. for whiting and 0.017, 0.036, 0.05, 0.29, and 6.4 mg/kg wet wt. for red mullet, respectively (Bat et al., 2020). Anyway the resulted levels proved lower than the permitted values set by EU legislation (EC, 2006).

Marmara Sea is connected through Bosphorus with Black Sea and is located south-west to it. Concentrations of Cd and Pb in the tested muscle and gills of ten commercially important marine fish species from Gulf of Gemlik were obtained elevated above the tolerance limits of European Union (EU) and the World Health Organization (WHO) standards. The highest concentrations of Cd was found in the gill tissue of *Sardinella maderensis*, *Solea vulgaris* and *Belone belone* (3.62, 3.46 and 3.05 $\mu g/g^{-1}$, respectively) and highest concentrations of Pb was determined in the gill tissues of *S. vulgaris* and *B. belone* (9.48 and 6.74 $\mu g/g^{-1}$, respectively), and the muscle tissue of *S. maderensis* (7.07 $\mu g/g^{-1}$) (Kayhan et al., 2017).

The aim of the study of Kuplulu et al., (2018) was to determined the concentrations of Cd, As, Pb and Hg levels in selected fish species from the Black, Marmara, Aegean and Mediterranean Sea. Different fish species mullet (*Mugil soiuy*), mackarel (*Trachurus trachurus*), seabass (*Dicentrarchus labrax*), shad (*Alosa fallax*), red mullet (*Mullus barbatus*), turbot (*Scophthalmus maximus*), anchovy (*Engraliusencrasicolus*), whitting (*Merlangius euxmus*), blue fish (*Pomatomus saltatrix*), bonito (*Sarda sarda*), grey mullet (*Mugil cephalus*), garfish (*Belone belone*), hake (*Merluccius merluccius*) have been obtained from the Black Sea. According to the results, metal concentrations decreased in the same order As>Pb>Hg>Cd in all the seas. Between the fish species, *Merluccius merluccius* has the highest concentrations of arsenic in the Marmara, Aegean and Mediterranean Sea; also this species has the second highest concentration of arsenic in the Black Sea.

It is essential to make comparison between heavy metal pollution in Black Sea with the neighbored Mediterranean Sea. The distribution of some heavy metals in the muscle tissue of whiting (*Merlangius merlangus*), red mullet (*Mullus barbatus*), anchovy (*Engraulis encrasicholus*) from Black and Mediterranean Sea was conducted by Turan et al. (2009). The highest Al (95.313 lg/g dw), Mn (1.390 lg/g dw), Zn (25.416 lg/g dw) concentration was detected in *E. encrasicholus* from Black Sea; the highest Li (3.200 lg/g dw) concentration was in *E. encrasicholus* from Mediterranean Sea; the highest Cd (1.685 lg/g dw) concentration was in *M. merlangus* from Mediterranean Sea; the highest Ni (1.363 lg/g dw) concentration was detected in *M. merlangus* from Black Sea; the highest Pb (0.727 lg/g dw) concentration was in *M. barbatus* from Black Sea and the highest Cr (1.893 lg/g dw), Fe (21.901 lg/g dw) concentration was detected in *M. barbatus* from Mediterranean Sea. The general conclusion could be that the relative isolation of Black Sea resulted in accumulation of higher amounts of metals in the marine biota.

Health risk assessment

Heavy metals pollution of marine ecosystems is of major environmental importance, but is essential primarily because of the impact on the health of fish consumers. Most of the above mentioned elements possess strong toxic effects and pronounced commutative abilities. Leading pathological capabilities possess Pb, Cd, As and Hg (Falco et al., 2006). This requires maximum allowable concentrations in seafood to be regulated by national, European legislation, World Health Organization and US Environmental Protection Agency (SG, 2004; 2008; EC, 2006; FAO/ WHO, 2003; 2010a; 2010b; WHO, 1993; 1996; USEPA, 1989; 2005). According to their recommendations the following assessments could be determined:

- *Tolerable Daily Intake* (TDI; mg/kg/day);
- *Provisional tolerable weekly intake* (PTWI; mg/kg of body weight);
- *Estimated weekly intake* (EWI; μg/kg/day);
- *Target hazard quotient* (THQ);
- *Total hazard index* (HI);
- *Target cancer risk* (TR).

The PTWI is defined as the estimated amount of a substance in food or drinking water, expressed on a body weight basis, that can be ingested weekly over a lifetime without appreciable health risk (WHO, 1993). The THQ values, developed by the USEPA (1989), have been recognized as useful parameters for human health risk assessment of metals associated with the intake of marine products. The THQ is also a non-carcinogenic risk assessment which is a ratio between the estimated dose of metal exposure and the oral reference dose. A THQ > 1 signifies that the level of exposure is higher than the oral reference dose, which assumes that a daily exposure at this level is likely to cause negative health effects during a lifetime in a human population (Bogdanovic et al., 2014). HI evaluates possible health effects that may be caused by the combination of all metals in the consumed seafood. For the risk assessment of multiple metals, the HI was calculated by summing all the calculated THQi values for the determined heavy metals. TR indicates carcinogenic risks (USEPA, 2005).

However European and Bulgarian legislation related to heavy metal pollution of marine hydrobionts determines the maximum permissible concentrations of only three particularly dangerous elements – Pb, Cd, Hg (Tabl. 1) (EC, 2006, SG, 2008).

This is all the more necessary given the fact that cooking methods (grilling, frying, boiling) could lead even to increased level of heavy metals in fish (Jailuang et al., 2019). It is of great importance to formulate mathematical description of the relation between water and sea organism pollution (Peycheva et al., 2017a). Furthermore, strict and continuous monitoring of marine ecosystems heavy metals pollution should be carried out in order to avoid harmful health impact.

Table 1: Maximum levels for certain contaminants in foodstuffs determined by (EC) No 1881/2006 of 19 December 2006

	LEAD	Maximum level (mg/kg wet weight)
1.	Muscle meat of fish	0,30
	CADMIUM	
1.	Muscle meat of the following fish, excluding species listed in 2, and 3.	0,050
2.	Muscle meat of the following fish: anchovy (Engraulis species) bonito (Sarda sarda)common two-banded seabream (Diplodus vulgaris), eel (Anguilla anguilla), grey mullet (Mugil labrosus labrosus), horse mackerel or scad (Trachurus species), louvar or luvar (Luvarus imperialis), sardine (Sardina pilchardus), sardinops (Sardinops species), tuna (Thunnus species, Euthynnus species, Katsuwonus pelamis), wedge sole (Dicologoglossa cuneata)	0,10
3.	Muscle meat of swordfish (Xiphias gladius)	0,30
	MERCURY	
1.	Fishery products and muscle meat of fish, excluding species listed in 2. The maximum level applies to crus-taceans, excluding the brown meat of crab and excluding head and thorax meat of lobster and similar large crustaceans (Nephropidae and Palinuridae)	0,50
2.	Muscle meat of the following fish:anglerfish (Lophius species), atlantic catfish (Anarhichas lupus), bonito (Sarda sarda), eel (Anguilla species), emperor, orange roughy, rosy soldierfish (Hoplostethus species), grenadier (Coryphaenoides rupestris), halibut (Hippoglossus hippoglossus), marlin (Makaira species), megrim (Lepidorhombus species), mullet (Mullus species), pike (Esox lucius), plain bonito (Orcynopsis unicolor), poor cod (Tricopterus minutes), portuguese dogfish (Centroscymnus coelolepis), rays (Raja species), redfish (Sebastes marinus, S. mentella, S. viviparus), sail fish (Istiophorus platypterus), scabbard fish (Lepidopus caudatus, Aphanopus carbo), seabream, pandora (Pagellus species), shark (all species), snake mackerel or butterfish (Lepidocybium flavobrunneum, Ruvettus pretiosus, Gempylus serpens), sturgeon (Acipenser species), swordfish (Xiphias gladius), tuna (Thunnus species, Euthynnus species, Katsuwonus pelamis).	**1.0**

Conclusion

- Limited research is available on the bioaccumulation of heavy metals from Bulgarian Black Sea coast fish.
- The heavy metal with highest concentration in almost all presented researches was Zn.
- Seasonal and geographical variations of heavy metals accumulation in marine biota are insufficiently evaluated.
- Reported elements content was within the legislation limit values and should not possess any hazard health risk.
- Bulgarian and European legislation determined maximum level only for some of the heavy metals in marine fish – Pb, Cd and Hg.
- However the possible heavy metals pollution dynamics requires constant and geographically extensive monitoring on the commercially important fish species.

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References

1. Akkoyunlu A. (2018). *Land-Based Pollution on the Black Sea along the Turkish Shoreline*. J Marine Sci Res Dev, 8:2.
2. Alkan A., Alkan N., Abaş U. (2016). *The Factors Affecting Heavy Metal Levels in the Muscle Tissues of Whiting (Merlangius merlangus) and Red Mullet (Mullus barbatus)*. Journal of Agricultural Sciences 22, 349–359.
3. Altas L., Buyukgungor H. (2007). *Heavy metal pollution in the Black Sea shore and offshore of Turkey*. Environ Geol 52:469–476.
4. Aygun S.F., Abanoz F.G. (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 Univ Vet Fak Derg17 (Suppl A): S145–S152.
5. Bakan G., Büyükgüngör H. (2000). *The Black Sea. Marine Poll*. Bull. 4:24–43.
6. Bat L., Arici E. (2016). *Health risk assessment of heavy metals in Sarda sarda Bloch, 1793 for people through consumption from the Turkish Black Sea coasts*. International Journal of Zoology Studies, Volume 1; Issue 1; January; pp. 01–07.
7. Bat L., Arici E., Sezgin M., Sahin F. (2017a). *Heavy Metal Levels in Commercial Fishes Caught in the southern Black Sea coast*. International Journal of Environment and Geoinformatics 4(2): 94–102, 94–102.
8. Bat L., Arici E., Ürkmez D. (2017b). H*eavy Metal Levels in the Black Sea Sprat (Sprattus sprattus)*. International Journal of Research in Agriculture and Forestry Volume 4, Issue 6, 2017, pp. 1–8.
9. Bat L., Öztekin A., Arici E., Şahin F. (2020). *Health risk assessment: heavy metals in fish from the southern Black Sea*. Foods and Raw Materials. 8(1):115–124.
10. Bat L., Öztekin A., Sahin F. (2018). *Heavy Metal Detection in Scorpaena Porcus Linnaeus, 1758 from Sinop Coast of the Black Sea and Potential Risks to Human Health*. Current Agriculture Research Journal, Vol. 6, No(3), pp. 255–260.
11. 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 15:393–399.
12. Bat L., Şahin F., Öztekin A. (2019). *Heavy metal contamination of Pleuronectiformes species from Sinop coasts of the Black Sea*. Sustainability, Agri, Food and Environmental Research, (ISSN: 0719–3726), 7(2):150–162.
13. Bat L., Sezgin M., Üstün F., Şahin 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.
14. Bogdanovic T., Ujevic I., Sedak M., Listes E., Simat V., Petricevic S., Poljak V. (2014). *As, Cd, Hg and Pb in four edible shellfish species from breeding and harvesting areas along the eastern Adriatic Coast, Croatia*. Food Chem. 146, 197–203.
15. Boran M., Altnok I. (2010). A *review of heavy metals in water, sediment and living organisms in the Black Sea*. Tr. J. Fish. Aquat. Sci. 10, 565–572.
16. Canli M., Atli G. (2003). *The relationships between heavy metal (Cd, Cr, Cu, Fe, Pb, Zn) levels and the size of six Mediterranean fish species*. Environ. Pollut. 121, 129.

17. Commission Regulation (EC). (2006). *Setting maximum levels for certain contaminants in food stuffs. Off. J. Euro. Union. Commission Regulation, No 1881/2006*:*364*. 5–24.
18. *Drainage Basin of the Black Sea*. source: https://www.unece.org/fileadmin/DAM/env/water/blanks/assessment/black.pdf, last visited: 14.04.2020.
19. Ergönül M.B., Altindağ A. (2014). *Heavy Metal Concentrations in the Muscle Tissues of Seven Commercial Fish Species from Sinop Coasts of the Black Sea*. Annual Set The Environment Protection. Volume 16, 34–51.
20. *Executive Agency for Fisheries and Aquaculture*. http://iara.government.bg/, last visited: 22.04.2020.
21. Falco G., Llobet J.M., Bocio A., Domingo J.L. (2006). *Daily Intake of Arsenic, Cadmium, Mercury, and Lead by Consumption of Edible Marine Species*. Journal of Agricultural and Food Chemistry, 54: 6106–6112.
22. FAO/ WHO. (2003). *Joint FAO/WHO Expert Committee on Food Additives. Food additives and food contaminants*. http://www.fao.org/fileadmin/templates/agns/pdf/jecfa/2003–02–24_Food_Add_Cont_Guidelines.pdf.
23. FAO/WHO. (2010a). *Joint FAO/WHO Expert Committee on Food Additives. Summary and conclusions of the seventy–third meeting of the JECFA. JECFA/73/SC, Geneva, Switzerland*. https://www.who.int/foodsafety/publications/chem/summary73.pdf.
24. FAO/WHO. (2010b). *Report of the Joint FAO/WHO Expert Consultation on the Risks and Benefi ts of Fish Consumption. Rome, Food and Agriculture Organization of the United Nations; Geneva, World Health Organization*. http://www.fao.org/3/ba0136e/ba0136e00.pdf
25. Fattorini D., Notti A., Di Mento R., Cicero A. M., Gabellini M., Russo A., Regoli F. (2003). *Seasonal, spatial and inter–annual variations of trace metals in mussels from the Adriatic Sea: A regional gradient for arsenic and implications for monitoring the impact of offshore activities*. Chemosphere, 72, 1524.
26. Jailuang S., Soikum C., Saipan P. (2019). *Effects of cooking methods on arsenic, cadmium, and lead in tilapia and human risk assessment*. KKU Veterinary Journal, Vol. 29 No. 2, 129–137.
27. Jakimska A., Konieczka P., Skóra K., Namieśnik J. (2011). *Bioaccumulation of Metals in Tissues of Marine Animals, Part II: Metal Concentrations in Animal Tissues*. Pol. J. Environ. Stud. Vol. 20, 1127–1146.
28. Jarup L. (2003). *Hazards of heavy metal contamination*. British Medical Bulletin, 68: 167–182.
29. Kayhan F.E., Büyükurganci N., Kaymak G. (2017). *Accumulation of Cadmium and Lead in Commercially Important Fish Species in the Gulf of Gemlik, Marmara Sea, Turkey*. Turkish Journal of Aquatic Sciences, 32(4): 178–183.
30. Kuplulu O., Iplikcioglu Cil G., Korkmaz S.D., Aykut O., Ozansoy G. (2018). *Determination of Metal Contamination in Seafood from the Black, Marmara, Aegean and Mediterranean Sea Metal Contamination in Seafood*. J Hellenic Vet Med Soc, 69(1):749–758.
31. Makedonski L., Peycheva K., Stancheva M. (2015). *Determination of some heavy metal of selected Black Sea fish species*. Food Control, 20, 1–6.
32. Peycheva K., Bangov I., Stancheva M. (2017a). *Mathematical description of the relation between water and sea organism pollution*. Bulgarian Chemical Communications, Volume 49, Special Issue D (pp. 271–274).
33. Peycheva K., Stancheva M., Georgieva S., Makedosnki L. (2017b). *Heavy Metals in Water, Sediments and Marine Fishes from Bulgarian Black Sea*. DOI:10.31519/conferencearticle_5b1b93d4d78bb6.88545986 Corpus ID: 132576151.

34. Radu G., Antona E., Golumbeanua M., Raykov V., Yankova M., Panayotova M., Shlyahov V., Zengin M. (2011). *State of the Main Black Sea Commercial Fish Species Correlated with the Ecological Conditions and Fishing Effort*. Journal of Environmental Protection and Ecology 12, No 2, 549–557.
35. Simionov I–A., Cristea V., Petrea S-M., Mogodan A., Nicoara M., Baltag E.S., 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*. J. Mar. Sci. Eng. 2019, 7, 466.
36. Stancheva M., Makedonski L., Petrova E. (2013a). *Determination of heavy metals (Pb, Cd, As and Hg) in Black Sea grey mullet (Mugil cephalus)*. Bulg. J. Agric. Sci., Supplement 1:30–34.
37. Stancheva M., Makedonski L., Peycheva K. (2014). *Determination of heavy metal concentrations of most consumed fish species from Bulgarian Black Sea coast*. Bulgarian Chemical Communications 46(1):195–203.
38. Stancheva M., Merdzhanova A., Petrova E., Petrova D. (2013b). *Heavy metals and proximate composition of Black Sea sprat (Sprattus sprattus) and goby (Neogobius melanostomus)*. Bulgarian Journal of Agricultural Science 19(1):35–41.
39. Stancheva M., Peycheva K., Makedonski L., Rizov T. (2010). *Heavy metals and PCBs level of bluefish (Pomatomus saltatrix) from Bulgarian black sea waters.* Ovidius University Annals of Chemistry, 21(1), 41–48.
40. State Gazette (SG). (2004). *Regulation of setting maximum levels of certain contaminants in foodstuff*. Number 31, 08 October 2004, Issues 88.
41. State Gazette (SG). (2008). *Regulation of settings maximum level for certain contaminants in foodstuffs*. 17 May 2008, Issue 26.
42. Stoyanova S., Sirakov I., Velichkova K., Staykov Y. (2015). *Chemical composition and content of heavy metals in the flesh of the different marine fish species*. J BioSci Biotechnol, 297–301.
43. Tchounwou P.B., Yedjou C., Patlolla K., Sutton D. (2012). *Heavy Metals Toxicity and the Environment*. Exs. 101: 133–164.
44. Tuncer G., Karakas T., Balkas T., Gokcay C., Aygun S., Yurteri C., Tuncel G. (1998). *Land-based sources of pollution along the Black Sea coast of Turkey: concentrations and annual loads to the Black Sea*. Mar Pollut Bull 36:409–423.
45. Turan C., Dural M., Oksuz A., Ozturk B. (2009). *Levels of Heavy Metals in Some Commercial Fish Species Captured from the Black Sea and Mediterranean Coast of Turkey*. Bull Environ Contam Toxicol, 82:601–604.
46. Uluozlu D., Tuzen M., Mendil D., Soylak M. (2007). *Trace metal content in nine species of fish from the Black and Aegean Seas, Turkey*. Food Chem., 104:835–840.
47. US Environmental Protection Agency (USEPA). (1989). *Guidance manual for assessing human health risks from chemically contaminated, fish and shellfish*. USEPA, Washington DC.
48. US Environmental Protection Agency (USEPA). (2005). *Guidelines for Carcinogen Risk Assessment Risk Assessment Forum*. U.S. Environmental Protection Agency Washington, DC
49. World Health Organization (WHO). (1993). *Guidelines for Drinking–water Quality. Volume 1, Recommendations. second ed*.
50. World Health Organization (WHO). (1996). *Trace elements in human nutrition and health. (NLM Classification: QU 130), Geneva*.