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Determination of heavy metal concentrations of most consumed fish species from Bulgarian Black Sea coast

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In this study some heavy metals (Cd, Ni, Cr, As, Hg Cu, Fe, Mn, Pb and Zn) concentration in edible parts of five most consumed Bulgarian fish species - bluefish (Pomatomus saltatrix), gray mullet (Mugil cephalus), Mediterranean horse mackerel (Trachurus mediterraneus ponticus), shad (Alosa pontica) and sprat (Sprattus sprattus sulinus) collected from two stations across Bulgarian Black Sea coast were determined. The samples were digested with nitric acid followed by appropriate spectroscopic determination (Atomic Emission Spectroscopy with Inductively Coupled Plasma (AES-ICP), Flame Atomic Absorption Spectroscopy (FAAS) or Electrotermal Atomic Absorption Spectroscopy (ETAAS). The level of As in the edible part of gray mullet (Mugil cephalus) has shown a value higher than limits set from various health organizations (1.1 ± 0.1 mg/kg). On the contrary this fish species accumulates the other investigated heavy metals such as Hg, Zn, Fe and Pb to lower extend. The concentration of Zn and Fe showed the highest value for all fish species. With some exceptions the concentration of studied heavy metal elements was within the acceptable levels for food source for human consumption.

Keywords: heavy metals; fish; Black Sea; Bulgaria

INTRODUCTION

The heavy metal pollution of the marine environment has long been recognized as a serious environmental concern [1, 2].

Heavy metals can be accumulated by marine organisms thought a variety of pathways, including respiration, adsorption and ingestion [3, 4]. Heavy metal contamination has been identified as a concern in coastal environment, due to discharges from industrial waste, agricultural and urban sewage [5, 6]. The levels of heavy metals are known to increase drastically in marine environment through mainly anthropogenic activities [7]. Heavy metals can be classified as potentially toxic (arsenic, cadmium, lead, mercury, nickel, etc.), probably essential (vanadium, cobalt) and essential (copper, zinc, iron, manganese, selenium) [8]**.** Fishes are good indicators for the long term monitoring of metal accumulation in the marine environment. Therefore, numerous studies have been carried out on metal accumulation in different fish species [9, 10].

There are limited data about heavy metals pollution of the Bulgarian Black Sea coast for the last twenty years [11]. Therefore the aim of this study was to determine the levels of cadmium, nickel, chromium, mercury, iron, manganese, copper, zinc, arsenic and lead in edible parts of five most consumed Bulgarian fish species collected from the coast of Black Sea.

The Black Sea is the world's largest natural anoxic water basin below 180 m in depth. It is a closed sea with a very high degree of isolation from the world's oceans, but it receives freshwater inputs from some of the largest rivers in Europe; the Danube, the Dniester, and the Dnieper [12]. For this reason, Black Sea is considered one of the most polluted seas, and the increasing concentration of nutrients in recent years have led to a higher degree of eutrophication. The fishery yield has declined dramatically, and the tourism industry also suffers from serious pollution of the Black Sea.

EXPERIMENTAL

Sampling and sample treatment

Samples of fish were randomly acquired in local fishermen from cities across the coastal waters of Bulgarian Black Sea. All the fish species were sampled from February to November 2010. These sampling sites of two regions of Bulgarian Black Sea coast – Varna and Bourgas (Fig. 1).

The five species (34 samples) included in this study are shown in Table 1. Total length and weight of the sample brought to laboratory on ice after collection were measured to the nearest millimeter and gram before dissection. For small species (i.e. sprat and Mediterranean horse mackerel), the entire edible part of each individual was included for preparation of composite sample. However, for

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Table 1. Biometrics data (mean ± SD) of fish from the coastal waters of the Bulgarian Black Sea

Sample	Sampling Location	Sampling season, year	N	Weight (g)± *SD*	Length (cm)± *SD*
Bluefish (Pomatomus saltatrix)	Bourgas	Autumn 2010	6	71.1±6.8	19.3±1.0
Gray mullet (Mugil cephalus)	Bourgas	Autumn 2010	6	335.0±1.2	32.1±0.8
Mediterranean horse mackerel (Trachurus mediterraneus ponticus)	Bourgas	Autumn 2010	6	10.8±5.3	9.7±1.4
Shad (Alosa pontica)	Varna	Spring 2010	6	195±3	29.5±1.3
Sprat (Sprattus sprattus)	Bourgas	Spring 2010	10	4.7±2.1	9.2±0.9

Fig. 1. The map of sampling locations in the Bulgarian Black Sea coast.

bigger species (i.e. gray mullet, bluefish and shad) only fillets of edible part of each individual were collected and included in the respective composite samples. Approximately 1 g sample of muscle from each fish were dissected, washed with distilled water, weighted, packed in polyethylene bags and stored at -18ºC until chemical analysis.

Reagents and standard solutions

All solutions were prepared with analytical reagent grade chemicals and ultra-pure water (18 MΩ cm) generated by purified distilled water with the Milli-QTM PLUS system. HNO_3 was of superb quality was purchased from Fluka. All the plastic and glassware were cleaned by soaking in 2 M HNO_3 for 48 h, and rinsed five times with distilled water, and then five times with deionised water prior to use.The stock standard solutions of Cd, Cr, Cu, Fe, Mn and Pb 1000 μg mL^{-1} were Titrisol, Merck in 2% v/v HNO_3 and were used for preparation calibration standards.

A DORM-2 (NRCC, Ottawa) certified dogfish tissues was used as the calibration verification standard. Recoveries between 90.5 and 108% were accepted to validate the calibration.

Sample digestion

Fish samples (whole fish body or fish fillets) are thoroughly washed with MQ water. The fish specimens were dissected and samples of fish fillets quickly removed and washed again with MQ water. Each fish filletes (approximately 1 g) were analyzed after homogenization in small mixer. To assess the total metal contents, microwave assisted acid digestion procedure was carried out. Microwave digestion system "Multiwave", "Anton Paar" delivering a maximum power and temperature of 800 W and 300°C, respectively, and internal temperature control, was used to assist the acid digestion process. Reactors were subjected to microwave energy at 800 W in five stages.

Instrumental

The samples were digested with nitric acid followed up by appropriate spectroscopy determination (Atomic Emission Spectroscopy with

Inductively Coupled Plasma (AES-ICP), Flame Atomic Absorption Spectroscopy (FAAS) or Electrotermal Atomic Absorption Spectroscopy (ETAAS)).

Determination of Cu, Fe and Zn: Flame atomic absorption spectrometric measurements were carried out on a Perkin Elmer (Norwalk, CT, USA) Zeeman 1100 B spectrometer with an air/acetylene flame. The instrumental parameters were optimized in order to obtain maximum signal-to-noise ratio.

Determination of As, Cd, Ni and Pb: Electrothermal atomic absorption spectrometric measurements were carried out on a Perkin Elmer (Norwalk, CT, USA) Zeeman 3030 spectrometer with an HGA-600 graphite furnace. Pyrolytic graphite-coated graphite tubes with integrated platforms were used as atomizers. The spectral bandpass, the wavelengths and instrumental parameters used were as recommended by the manufacture. Only peak areas were used for qualification. Pd as $(NH_4)_2PdCl_4$ was used as modifier for ETAAS measurements of As and Cd.

Determination of Hg was performed by Milestone DMA-80 direct Mercury Analyzer.The sample size is between 0.020 and 0.0060 g, with drying temperature at 300°C for 60 sec, decomposition time -180 sec an waiting time 60 sec.

Statistical analysis

The whole data were subjected to a statistical analysis. Student's-test was employed to estimate the significance of values.

RESULTS AND DISCUSSION

Levels of heavy metal in the muscle of fish species from coastal waters of Bulgarian Black Sea are shown in Table 2.

The summarized results of this study are expressed as means (mg/kg) fresh weight.

Cadmium is a non-essential, highly toxic metal. Chronic effects on human health may occur as a result of its accumulation in liver, bones, blood, kidney and muscle [13]. About 50% of the Cd that reaches the sea comes from human activities (industrial waste, fertilizers containing phosphate or animal origin, etc.). The European Community [14] established the maximum levels permitted of cadmium in a fish as 0.05 mg/kg f.w. Moreover, the Joint Food and Agriculture Organization and World Health Organization (FAO/WHO) [15] has recommended the provisional tolerable weekly intake (PTWI) as 0.007 mg/kg body weight for cadmium. The maximum Cd level permitted for fish samples is 0.10 mg/kg according to Turkish Food Codex [16]. The Bulgarian Food Regulation recommends a 0.05 mg/kg f.w. for sea fish [17]. Cadmium levels in analyzed fish species were below 0.010 mg/kg fresh weight for muscle except gray mullet – 0.012 mg/ kg f.w . Cadmium concentration in literature has been reported as follow: 0.02-0.24 mg kg^{-1} for gray mullet [18]; from 0.10 µg/g in Psetta maxima; up to 0.35 µg/g in Mugil cephalus; 0.23 µg/g for Pomatomus Saltator; 0.13 µg/g for Sarda Sarda; 0.32 µg/g for Trachurus trachurus; 0.30 µg/g for Sprattus sprattus from the Black Sea, Turkey [19]; 0.02-0.37 mg kg^{-1} for edible part of fishes caught from Marmara, Aegean and Mediterranean seas in Turkey [20] and 0.002-0.02 mg Cd kg^{-1} fresh weight for species from Adriatic Sea [21]. In the present study, cadmium levels (Fig. 2) were in good agreement with

Table 2. The mean heavy metal concentration (mg/kg f.w.) in the tissues of the examined species from Bulgarian Black Sea coast

Species		Cd		Ni		Cr		As		Hg		Zn		Cu		Fe		Mn		Pb	
		mean	SD	mean	SD	mean	SD	mean	SD	mean	SD	mean	SD	mean	SD	mean	SD	mean	SD	mean	SD
Bluefish	**fillet**	0.008	0.001	0.009	0.001	0.06	0.01	0.77	0.06	0.09	0.01	10	1	0.8	0.1	5.0	0.4	0.08	0.01	0.03	0.01
Gray mullet	**fillet**	0.012	0.002	0.009	0.001	0.07	0.01	1.1	0.1	0.05	0.01	5.2	0.3	0.34	0.02	2.2	0.2	0.17	0.01	0.05	0.01
Medi - terranean horse mackerel	**whole fish**	0.008	0.001	0.008	0.001	0.03	0.01	0.73	0.05	0.16	0.02	8.5	0.6	0.56	0.04	4.2	0.3	0.06	0.01	0.06	0.01
Shad	**fillet**	0.007	0.001	0.07	0.01	0.05	0.01	0.38	0.02	0.08	0.01	9	1	0.45	0.03	9	1	0.11	0.01	0.05	0.01
Sprat	**whole fish**	0.005	0.001	0.028	0.003	0.04	0.01	0.73	0.04	0.12	0.02	11.0	0.7	1.40	0.08	9	1	0.11	0.01	0.08	0.02

At $p < 0.05$

reported literature data and with the data from the international organizations.

The highest total lead content was found in sprat (Sprattus sprattus), 0.08 ± 0.02 mg Pb kg^{-1} fresh weight, while the lead content for the other fish samples were below 0.06 mg/kg (Fig. 3).

Lead is one of the most ubiquitous and useful metal known to humans and it is detectable in practically all phases of the inert environment and in all biological systems [22]. The Joint FAO/WHO

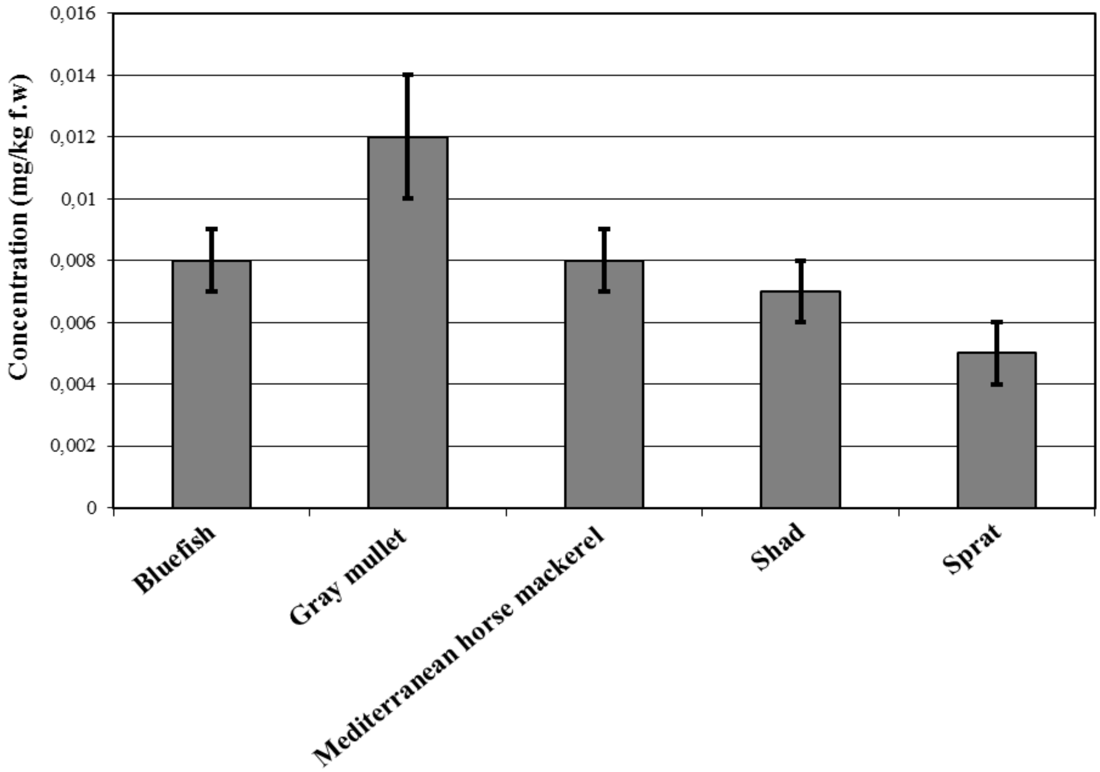

Fig. 2. Distribution of Cd in fish species from Bulgarian Black Sea coast.

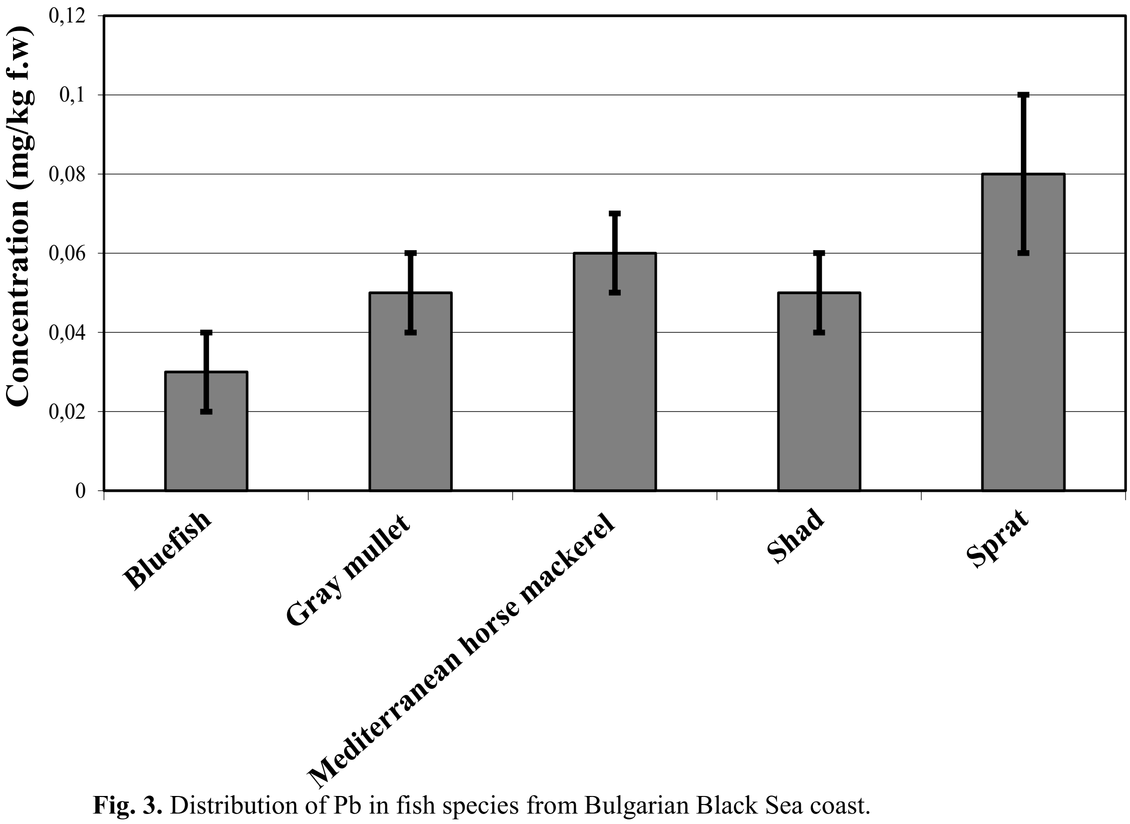

Fig. 3. Distribution of Pb in fish species from Bulgarian Black Sea coast.

[23] Expert Committee on Food Additives establishes a provisional tolerable weekly intake (PTWI) for lead as 0.025 mg/kg body weight. Whereas the maximum level of lead in seafood establishes by the European Community [14] is 0.2 mg/kg f.w in fish. According to Turkish Food Codex, the maximum lead level permitted for sea fishes is 0.3 mg/kg [16] while Bulgarian Food Regulation sets this level as 0.4 mg/kg fresh weight (for sea fish) [17]. Lead levels in the literature have been reported in the range of 0.22-0.85 mg kg^{-1} for muscle of fish from the middle Black Sea [24], 0.28 µg/g in Psetta maxima and 0.87 µg/g in Pomatomus Saltator from the Black Sea, Turkey [19], 0.33-0.93 µg kg^{-1} for muscle of fish from Black and Aegean seas [25] and in between 0.14 and 1.28 µg kg^{-1} for fish muscle from Aegean and Mediterranean seas [26]. The values obtained from the analyzed samples showed good agreement with values reported in the literature and below the level set by various health organizations.

Arsenic, a naturally occurring element, is a worldwide contaminant that is found in rock, soil, water, air and food. Arsenic is highly toxic element. Humans can be exposed to arsenic through the intake of food and drinking water, but for most people, the major exposure source is the diet, mainly fish and seafood [22]. Arsenic concentration in this study ranged between 0.38 mg kg^{-1} in shad (Alosa pontica) from north up to 1.1 mg kg^{-1} in gray mullet (Mugil cephalus) from south.

There are limited data about the arsenic content in fish species in the literature. The Joint FAO/WHO [27] Expert Committee on Food Additives (JECFA) establishes a provisional tolerable weekly intake (PTWI) for inorganic arsenic as 0.015 mg/kg body weigh/week and 0.05 mg/kg body weigh/week for organic-arsenic intakes. The maximum arsenic level permitted for fishes is 1.0 mg/kg according to Australian standards [28]. The concentration of arsenic reported in fish species from Adriatic Sea ranged of 0.56 to 10.03 mg As kg^{-1} fresh weight [21] and in Lake Kasumigaura, Japan was around 13.3 µg g^{-1} dry wt for fish food [29]. Tuzen [19] had measured an arsenic concentration in different fish species from Black Sea as follows: 0.15 ± 0.01 µg/g for Psetta maxima; 0.27 ± 0.02 µg/g for Pomatomus Saltator, 0.23 ±0.01 µg/g for Mugil cephalus, 0.14 ± 0.01 µg/g for Sarda Sarda, 0.18 ± 0.02 µg/g for Trachurus trachurus and 0.17 ±0.01 µg/g for Sprattus sprattus. The concentration of As in this study (Fig. 4) was generally low in all the species compared with both the data in the literature and world food standards except the value for gray mullet (Mugil cephalus).

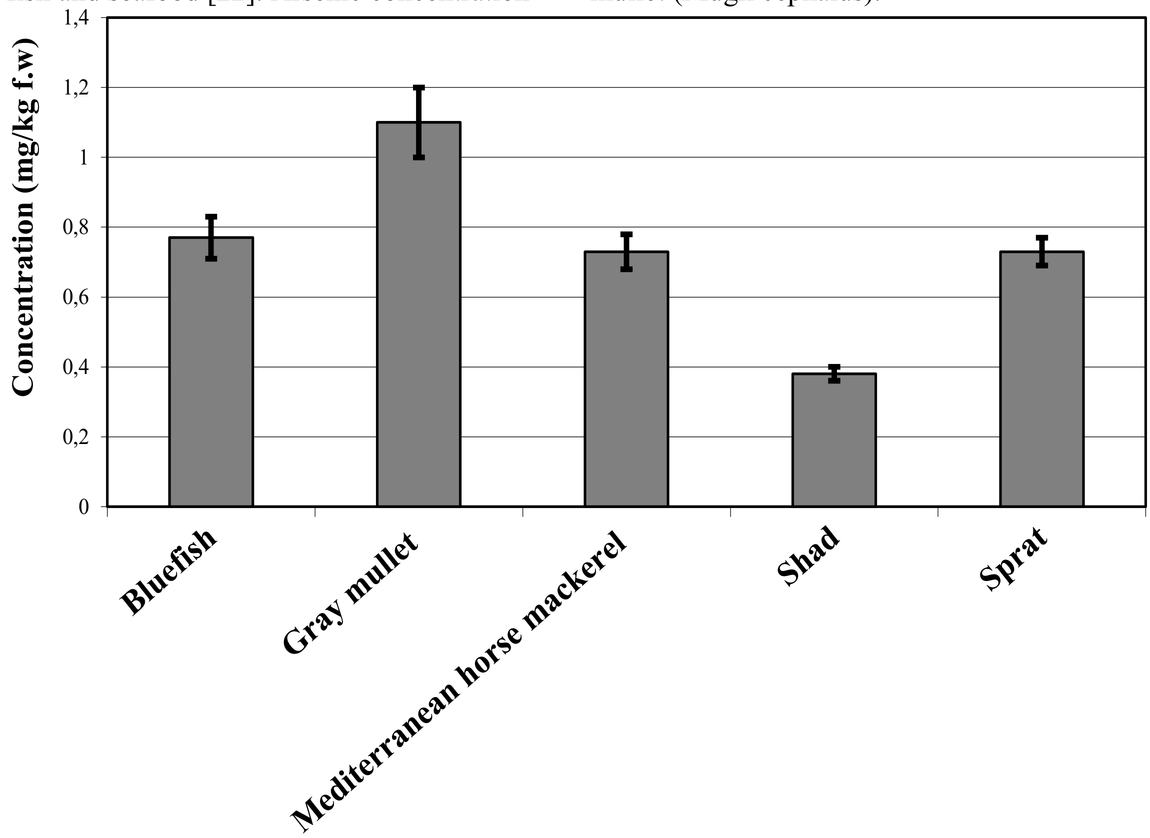

Fig. 4. Distribution of As in fish species from Bulgarian Black Sea coast.

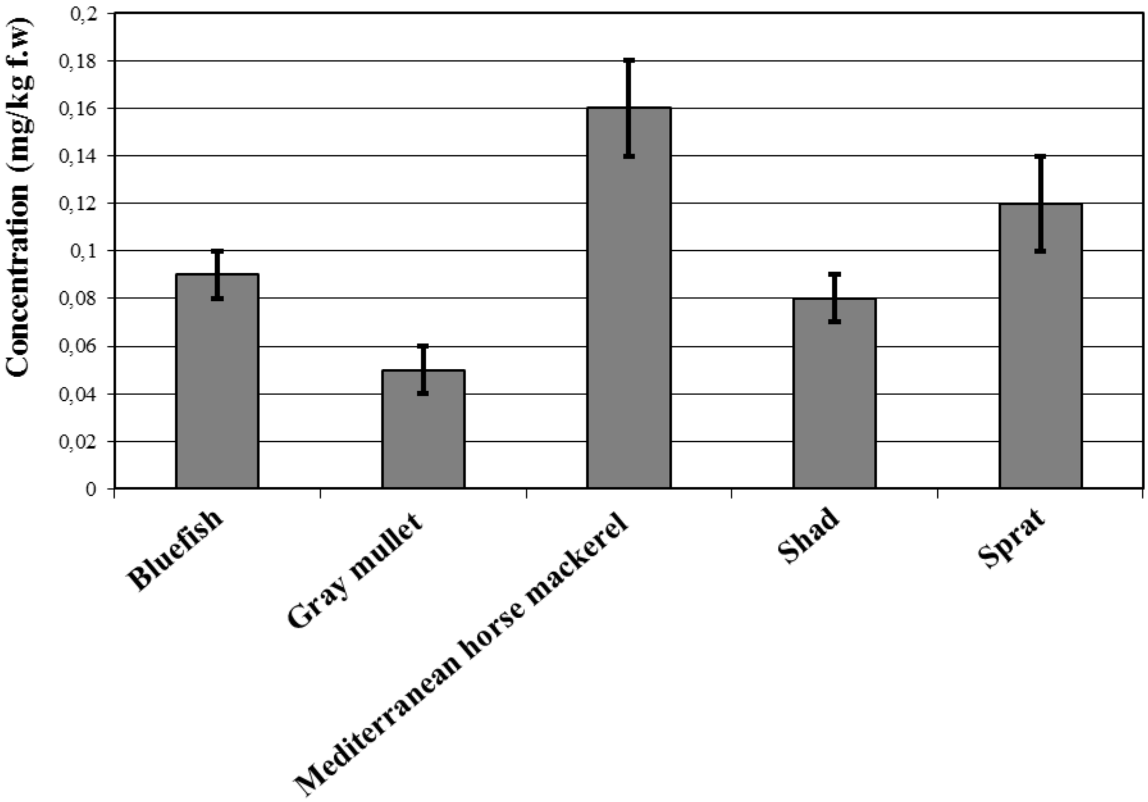

Fig. 5. Distribution of Hg in fish species from Bulgarian Black Sea coast.

The lowest and highest mercury levels in fish species were found as 0.05 mg/kg in Mugil cephalus and 0.16 mg/kg in Trachurus mediterraneus ponticus (Fig. 5). The maximum Hg level permitted for fishes is 0.5 mg/kg according to Turkish Food Codex [16] and Bulgarian Food Codex [17]. The PTWI is 5 mg total mercury kg^{-1} body weight (bw) and 3.3 mg methylmercury kg^{-1} bw [30] was reduced to 1.6 mg methylmercury kg^{-1} bw [31] and could be exceeded depending on the species and quantity consumed. Mercury levels in analyzed fish samples were found to be lower than legal limits. In the literature mercury levels in fish samples have been reported in the range of 0.01-0.50 μg/g in marine fishes in Malaysia [32], 0.02-0.74 mg/kg wet weight in canned fishes [33], 25-84 μg/kg for fishes from Black Sea [19]. In humans, mercury is toxic to the developing fetus and considered a possible carcinogen [34]. Mercury is a known human toxicant and the primary sources of mercury contamination in man are through eating fish [35].

Copper is essential for good health but very high intake can cause adverse health problems such as liver and kidney damage [36]. The copper concentration found in this study was in the range of 0.34 up to 1.4 mg kg^{-1}. Copper in the literature range from 0.23 to 9.49 mg kg^{-1} for muscle of fish from Marmara Sea [37], 0.32-6.48 mg kg^{-1} for muscle of fish from Marmara, Aegean and Mediterranean seas in Turkey [20] and 0.34-7.05 mg kg^{-1} wet weight for fish muscle from central Aegean and Mediterranean Sea [26]. The minimum and maximum copper levels in fish species from Black Sea, Turkey were found as 0.65 μg/g in Trachurus trachurus and 2.78 μg/g in Pomatomus Saltator [19]. The maximum copper level permitted for sea fishes is 10 mg/kg according to Bulgarian Food Authority [17] and 20 mg/kg according to Turkish Food Codex [16]. The Joint FAO/WHO [23] Expert Committee on Food Additives established the provisional tolerable weekly intake (PTWI) for copper of 3.5 mg/kg body weight/ week. Our values were lower than the values from the literature.

Zinc is known to be involved in most metabolic pathways. Deficiency of this essential element most often occurs when intake of zinc is inadequate or if there is poor absorption by the body. The minimum and maximum zinc levels in fish were found as 5.2 mg Zn kg^{-1} in Mugil cephalus and 11 mg Zn kg^{-1} in Sprattus sprattus from Bourgas station.

The concentration for zinc reported in the literature range of 9.5-22.9 mg kg^{-1} for muscle of fish from the Black Sea coast [18], 16.1-31.4 mg

kg^{-1} for muscles of fish from Mediterranean sea [38], 3.51-53.5 mg kg^{-1} for species from Aegean and Mediterranean Sea [26], 9.50-22.94 µg/g dry weigh for fish muscle from middle Black sea [24], and 38.8 µg/g - 93.4 µg/g for different types of fishes from Black Sea, Turkey [19]. The maximum zinc level permitted for fishes is 50 mg/kg according to Bulgarian Food Codex [17] and Turkish Food Codex [16]. The Joint FAO/WHO [23] Expert Committee on Food Additives established the PTWI for zinc of 7 mg/kg body weight/week. Maximum Zn level in edible parts of fish in this research was found to be below than both the Turkish permissible standards and levels reported in the literature.

Manganese is an essential element for all known living organisms. Manganese deficiency diseases are very striking ranging from severe birth defects, asthma, convulsions and etc. The lowest and highest levels in fish species were found in Mediterranean horse mackerel (0.06 mg/kg) and in Mugil cephalus. Manganese contents in the literature have been reported in the range of 1.56-3.76 µg/g dry weight in fish samples of the middle Black Sea (Turkey) [24], 0.05-4.64 µg/g dry weight in fish species from Iskenderun Bay, Northern East Mediterranean Sea, Turkey [39] and 0.69-3.56 mg kg^{-1} for muscles of fish from the Black Sea coasts [18]. According to both FAO [40] and Bulgarian standards [17] there is no information on the carcinogenity of manganese. The concentration of manganese in our study was generally in agreement with the literature.

Iron levels ranged from 2.2 mg/kg fresh weight in Trachurus mediterraneus ponticus up to 9.0 mg/kg fresh weight for Alosa pontica and Sprattus sprattus. Iron concentration in the literature were reported between 59.6 and 73.4 mg kg^{-1} for muscles of fish from Mediterranean sea [38], 30-160 mg kg^{-1} for muscles of fish from the Black Sea coasts [18] and 9.52-32.40 µg/g dry weight in fish samples of the middle Black Sea (Turkey) [24]. The US National Academy of Science [41] recommends a Recommended Dietary Allowance (RDA) for iron in elderly women and men - 10 mg/day. There is no information about the maximum permissible iron concentration in fish tissues in Bulgarian standards [17]. Iron is an essential mineral that plays an important role in the human physiology. High Fe absorption causes excessed Fe to be stored in the organs, eventually leading to iron overload. Results achieved in this study were in good agreement with other reported data from the literature.

The lower chromium content was 0.03 mg/kg in Trachurus mediterraneus ponticus while the highest chromium content was 0.07 mg/kg in Mugil cephalus. Chromium is an essential mineral in humans and has been related to carbohydrate, lipid, and protein metabolism. The recommended daily intake is 50-200 µg [41]. The amount of chromium in the diet is of great importance as Cr is involved in insulin function and lipid metabolism [42]. The maximum Cr level permitted for fishes is 0.3 mg/kg according to Bulgarian Food Codex [17] and 0.1 mg/kg according to Brazil Standard [43]. Chromium contents in the literature have been reported in the range of 0.07–6.46 µg/g dry weight in fish species from Iskenderun Bay, Northern East Mediterranean Sea, Turkey [39], 0.04-1.75 µg/g in seafood from Marmara, Aegean and Mediterranean seas in Turkey [20], 1.42 µg/g in fish feed [34]. Our values are under those reported in the literature.

The lowest and highest nickel levels in fish species were 0.008 mg/kg in Sprattus sprattus and 0.07 mg/kg in Alosa pontica. Nickel contents have been reported in the range of 0.11-12.9 µg/g dry weight in fish species from Iskenderun Bay [39], 0.93-2.77 µg/g dry weight in fish samples from Dhanmondi Lake, 0.42-0.85 µg/g in canned fish [25], 1.14-3.60 µg/g in fishes from Black Sea, Turkey [19] and 0.02-3.97 µg/g in seafood from Marmara, Aegean and Mediterranean seas in Turkey [20]. The World Health Organization [13] recommends 100-300 µg nickel for daily intake. The maximum nickel level permitted for fishes is 0.5 mg/kg according to Bulgarian Food Codex [17]. The results from this study were below the limits sets by various health organizations and the data in the literature.

CONCLUSION

Heavy metals (Cd, Pb, As, Hg, Ni, Cu, Mn, Zn, Fe and Cr) were determined in five most consumed Bulgarian fish species collected from Bulgarian coastal of Black Sea. Among the ten metals under study, iron and zinc showed the highest level of accumulation. None the less this value was in the range stated in the literature. The levels of arsenic in gray mullet were higher than the other fish species but in within the recommended legal limits. In the analyzed fishes, there were no health risks in respect to the concentration of cadmium, copper, lead, mercury and other elements' level.

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ОПРЕДЕЛЯНЕ НА КОНЦЕНТРАЦИИТЕ НА ТЕЖКИ МЕТАЛИ В НАЙ-КОНСУМИРАНИТЕ РИБНИ ВИДОВЕ В БЪЛГАРСКОТО ЧЕРНОМОРСКО КРАЙБРЕЖИЕ

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(Резюме)

В настоящата работа са определени концентрациите на някои тежки метали (Cd, Ni, Cr, As, Hg, Cu, Fe, Mn, Pb and Zn) в едливите части на пет най-разпространени рибни видове - лефер (*Pomatomus saltatrix*), кефал (*Mugil cephalus*), средиземноморски сафрид (*Trachurus mediterraneus ponticus*), карагьоз (*Alosa pontica*) и цаца (*Sprattus sprattus sulinus*), събирани на две станции по българското черноморско крайбрежие. Пробите са третирани с азотна киселина със следващо спектроскопско определяне (атомно-емисионна спектрометрия с индуцирана плазма (AES-ICP), пламъкова атомна абсорбционна спектрометрия (FAAS) или електротермична атомна абсорбционна спектрометрия (ETAAS). Нивото на арсена в едливите части на кефала (*Mugil cephalus*) показват стойности, по-високи от допустимите според различните здравни организации (1.1 ± 0.1 mg/kg). Този рибен вид натрупва в по-ниска степен други изследвани метали, като Hg, Zn, Fe и Pb. Концентрациите на Zn и Fe показват най-високи стойности за всички рибни видове. С някои изключения концентрациите на изследваните тежки метали са в границите на приемливите нива за храни за консумация.