Environmental contamination by Zinc and the risk of its introduction into the food chain

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Abstract

Zn accumulation may be utilized as a reliable biomarker for determining the degree of environmental pollution in water, sediment, and river fish tissues. In this study data obtained from ICP-MS evaluation revealed that the levels of Zn in the sediment from 9 hotspots (HS) were: 214.5, 138.8, 164.8, 269.6, 156.6, 356.6, 120.8, 387.5, and 259.7 mg/kg dry mass of sediment, respectively. Zn concentrations in *S. cephalus* fish liver at 9 hotspots were as follows: 11.623, 9.982, 13.514, 31.451, 27.513, 39.791, 10.034, 46.502, and 14.903 mg/kg wet weight. Only in the HS-8 the Zn concentration in the liver exceed the FAO limits. Zn concentrations in muscle varied from HS-1 to HS-9: 3.013; 7,021; 3,304; 6,513; 5,504; 2,802; 5,213; 6.342; and 8.704 mg/ kg wet weight. The Zn concentrations in muscle did not surpass FAO guidelines and do not constitute a concern to public health. There is a statistical relationship between Zn concentration in sediment and the liver. The Zn level found in the sediment at each of the nine sampling locations, reveals heavy pollution caused by industry or other activities conducted in these locations and needs more serious attention from authorities.

Key words: *wild fish; tissues; Scualius cephalus; sediment; Vardar River*

Introduction

Increased human activity has resulted in significant pollution, posing a serious environmental concern to humans, invertebrates, and fish (Copaja et al., 2017). Heavy metals represent a major fraction of contaminants that accumulate in the food chain (Ahmad et al., 2014). Zn as an fundametal metal in low concentrations is necessary for the development and growth of aquatic organisms (Wang et al., 2000). The catalytic role of Zn is very important for critical biological functions catalyzed by more than 300 enzymes (McCall et al., 2000; Lall and Kaushik, 2021).

The exposure to high levels of Zn as well as its consumption directly through the food chain, is dangerous for the aquatic organisms and also for public health. High levels of Zn in water can be extremely toxic to aquatic organisms

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such as fish (Hogstrand, 2011). When the body is exposed to high levels of Zn, the liver is not able to metabolize its excessive amounts, and thus Zn (especially Zn^{2+} which is more toxic), can be transported through the blood to other organs of the body (Lall and Kaushik, 2021). Bioaccumulation of heavy metals in the tissues of aquatic organisms, including fish, can be used as an indicator of environmental contamination (Kucuksezgin et al., 2006; Bawuro et al., 2018). The gills are the primary entrance point for dissolved compounds from water, however, because of blood flow from the gills, the liver is more likely to receive heavy metals (Copaja et al., 2017). It is also crucial to note that only a small portion of free metal ions remain dissolved in water, while the majority are deposited in sediment as a result of hydrolysis and adsorption (Bradl, 2004).

The Vardar River is located in the Balkan Peninsula and drains southern Serbia, about 80% of the Republic of North Macedonia, and sections of northern Greece (Milovanovic, 2007). Several sources of Zn contamination are directly and indirectly related to the Vardar River basin. The primary sources of environmental pollution, including the contamination of water, sediment, and fish tissues, which allows for its introduction into the food chain and poses issues for public health, are the agriculture sector, the Zn processing industry, or various processes that use Zn (Ministry of Environment, 2009; Anim-Gyampo, 2013). According to the Food and Agriculture Organization (FAO), the permitted limit for Zn in fish tissues are 40 mg/kg weight of fresh fish (FAO, 1983). Meanwhile, Zn concentrations in sediment are evaluated by the US EPA (1996). Depending on the quantity of Zn concentration the level of pollution is categorized as high pollution occurs when the Zn content in the sediment exceeds 80 mg/kg dry matter, moderate pollution is in the range of 35-80 mg/kg dry weight, and no significant pollution when the Zn concentration in the sediment is less than 35 mg/kg dry weight (Baharom and Ishak, 2015).

S. cephalus is found across Europe, as well as the Black Sea, Caspian Sea, and Azov Sea basins (Özcan and Serdan, 2019). The species *S. cephalus* is quite widespread in the Vardar River basin, it is most often caught by amateur fishermen. Based on the above, we considered that fish of the *S. cephalus* species can be taken as reliable indicators of environmental pollution and the pollution of aquatic organisms of the Vardar River. The present study aimed to determine the concentration of Zn in the sediment and the tissues of wild fish belonging to the genus *Squalius cephalus* residing in the Vardar River in North Macedonia. By analyzing the concentration of Zn in the sediment and the tissues of *S. cephalus* and comparing the results with the guidelines and limits set by international organizations we can conclude for the levels of Zn contamination in the food chain.

Materials and methods

Study area

Sampling was carried out in the period July-August (2015) in 9 different locations presented in Figure 1, with the distance between them around 33 km along the Vardar river.

Samples consisted of *S. cephalus* fish (Figure 2) and sediment.

Six fish were sampled from each location with the assistance of a certified fisherman from the North Macedonian Fishing Federation.

Figure 1. The map of coordinates' sampling sites along the Vardar River

HS-1. Location before the Bistrica River flows into the Vardar River
HS-2. Location after the discharge of the Bistrica River into the Vardar River.
HS-3. Saraj location, located before the entrance of the Vardar River to the city of Skopje.
HS-4. Location Jurumleri, located at the outlet of the Vardar River from the city of Skopje.
HS-5. Location at the outlet of the Vardar River from the city of Veles.
HS-6. Location before the confluence of the Bregalnica River into the Vardar River (near Gradsko settlement).
HS-7. Location after the discharge of the Bregalnica River into the Vardar River (near Gradsko settlement).
HS-8. Location at the exit of the Vardar River from the city of Demir Kapija.
HS-9. Location before crossing the Vardar River in the territory of the Republic of Greece.

Figure 2. *Squalius cephalus*

Sampling

Fish samples were wrapped in ice and transferred to the authorized laboratory in portable freezers. Following that, the samples were packed in plastic bags with the date of catch, name of species, and tissues of fish documented and kept in the freezer at a temperature of -20 °C until the material was thawed and prepared for further analysis.

Sediment samples were collected at the same locations by the method described by APHA (2005). Three samples were collected at a distance of 500 m, with a volume of 500 mL of sediment at a depth of 3-4 cm in 9 different locations 30-33 km distance from each other.

Reagents, standards and method of validation

A mix standard solution for ICP MS was prepared (The periodic table Mix 1 for ICP, 10 mg/L, Sigma Aldrich, Munich, Germany) containing 33 elements (Al, Si, Ba, Be, Bi, B, Cd, Ca, Cs, Cr, Co, Cu, Ga, In, Fe, Pb, Li, Mg, Mn, Ni, P, K, Rb, Se, Si, Ag, Na, SR, S, Te, Tl, V, and Zn). For the calibration curve a single standard solution were used for: Ti, Ge, SB, Sn, and Mo (10 ppm in 10% HNO_3, Sigma Aldrich, Munich, Germany).

Solutions were prepared by selecting the required solvents. Ultra-pure nitric acid (HNO_3, 69.0% w/w, Sigma Aldrich, Munich, Germany), and hydrogen peroxide H_2O_2 (69.0% w/W, Sigma Aldrich, Munich, Germany) were used in a mixture for total digestion of samples. Standard Rhodium (1 mg/L, Sigma Aldrich, Munich, Germany) was used as an internal standard for the correction of the external calibration curve. Water bi distillate was used (0.065 μS/cm), which was prepared from the TKA Microlab water purification system, ASTM Type II (Thermo Electron LED GmbH, Germany) described according to Balabanova et al. (2015).

The validation method was done using calculation of the limit of detection and quantification, linearly, uncertainty, as well as the accuracy and precision of the measurements as described by Balabonova et al. (2015).

Fish sample digestion

Initially, all the frozen samples were allowed to defrost at room temperature before proceeding with the preparation of the samples for the digestive process. The wet digestion procedure was applied to all types of biological materials.

0.5 g of organic material was used for digestion, afterwards, 5 mL of HNO_3 was added and 2 mL of H_2O_2 before microwaving. Following digestion, the containers were left to cool until the (utensil) pressure dropped below 50 Psi and the temperature dropped below 40°C. The lid of each container was carefully removed and the contents were filtered in 25 mL volumetric flask and diluted with deionized water until mark and stored in a polyethylene container before Zn determination by Inductive Coupled Plasma Mass Spectrometry with the standard system Agilent 7500cx ICP-MS with a concentric nebulizer glass that was used for all analyses according to Balabanova et al. (2015) and Ducos et al. (2010).

Sediment digestion

The sediment digestion was conducted according to U.S EPA (1996). Sediment drying was performed in the microwave at 700°C for 72 hours. The material was then cooled and macerated in a porcelain mortar and crushed by compaction to fineness. After that it was placed in a polyurethane bag, and coded with the numbers of samples according to the location from which they were collected. 3 g of each sample was taken with analytical

scales and placed in a glass test tube for dilution with the so-called royal solution (21 mL HCl + 7 mL HNO_3). Afterward, the test tube was placed in a heat source (special electric stoves) for digestion. The digestion process was held at different temperatures with different durations: At 500°C for 10 minutes, at 700 °C for 10 minutes, at 900°C for 10 minutes, at 1100°C for 10 minutes, at 1200°C for 15 minutes, at 1300°C for 15 minutes, at 1400°C for 15 minutes, at 1500°C for 15 minutes and 1600°C for 120 minutes. After cooling, the material was subjected to preparation for analysis by adding H_2O_2 and filtered with filter paper. Subsequently, the solution was placed in a plastic container for ICP-MS analysis.

Standard analysis with ICP-MS

The analyses were performed at the Goce Delchev University-Stip in the Republic of North Macedonia with the standard system Agilent 7500 cx ICP-MS with a concentric nebulizer glass that was used for all analyses according to Ducos et al. (2010) and Balabanova et al. (2015).

Statistical analyses

The data were statistically analyzed using Excel 2013, the T-test was performed to compare heavy metal, and Paired Two Sample for comparison of variances was utilized. Stat graphics Centurion XVII, ANOVA, analysis of variance, and simple regression analysis were also applied.

Results

Table 1, reveals the results of Zn concentration in the tissues (muscles and liver) of the evaluated fish samples.

Results (table 1) show that the Zn concentration not only varies regarding the tissues but also within various locations in the same tissue. Within the liver, in HS no: 4, 5, 6, and 8, the Zn concentration is 31.451, 27.513, 39.791, and 46.502 mg/kg wet weight, respectively. The minimum concentration of Zn in the liver is in HS-2 (9.982 mg/kg wet weight), and the highest concentration of Zn is in HS-8 (46.502 mg/kg wet weight).

According to Bawuro et al. (2018) the MRL for Zn in wet fish is different from FAO and WHO during the years they are in the range 30 to 100 mg/kg wet weight (FAO 1983a; FAO 1983b; FAO/WHO 1989). We refer to the limits of Zn, 40 mg/kg wet weight of fish tissues (FAO 1983a).

Table 1. Zn concentration in liver and muscle (mg/kg wet weight) in *S. cephalus* fish

HS	Liver	Muscle
1	11.623	3.013
2	9.982	7.021
3	13.514	3.304
4	31.451	6.513
5	27.513	5.504
6	39.791	2.802
7	10.034	5.213
8	46.502	6.342
9	14.903	8.704

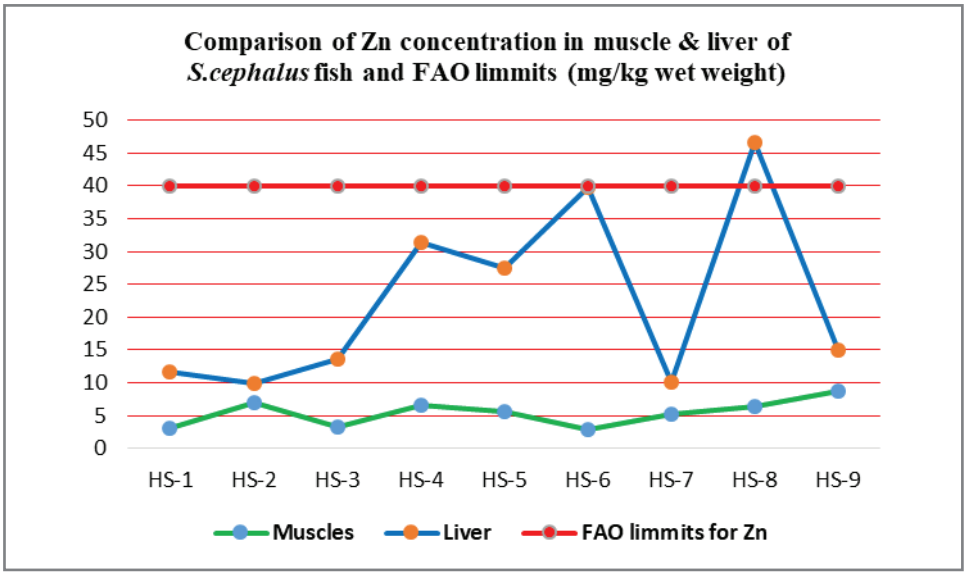

Figure 3. Zn concentration in liver, *S. cephalus* fish muscle and FAO limits (mg/kg wet weight)

In figure 3, we can see the Zn concentration in liver, muscle of *S. cephalus* fish, and FAO limits (mg/kg wet weight).

Except for location No. 8, where the Zn concentration in the liver is higher than the FAO limits (46.502 mg/kg wet weight compared to the limit of 40 mg/kg wet weight), it appears that the concentration of Zn in the tissues of fish of the *S. cephalus* fish tissue species is lower than the FAO limits.

In the nine hotspots from which samples were collected for our investigation, the Zn concentration in sediment was ranged from 120.8 mg/kg the lowest level to 387.5 mg/kg the highest level, with an average of 229.6 mg/kg, as shown in Figure 4.

The standard deviation is 95.46 and seems that is an extremely high, while 41.56 is the coefficient of variation. Zn thus exhibits high homogeneity in the nine HS from which the samples of sediment were obtained.

As it is seen HS-6 and HS-8 have the highest values when compared with the other HS. The lowest concentration was determined in HS-7, 120.8 mg/kg dry mass.

Discussion

Obtained data shows that the Zn concentration in the liver is higher than in the muscles (table 1). Similar studies have stated similar results regarding the higher concentration of Zn in the liver compared to its concentration in muscles (Muiruri et al., 2013; Aktas et al., 2016; Nastova et al., 2017). Also, Gale et al. (2004), and Nastova et al. (2017) stated that there is a Zn concentration in liver, kidneys, and other internal organs. Although, the results of Zn concentration in the liver of *S. cephalus fish liver in the this study* are lower than the above-mentioned results. In another study, Zn concentration was seasonally evaluated in different tissues of *Tinca tinca*

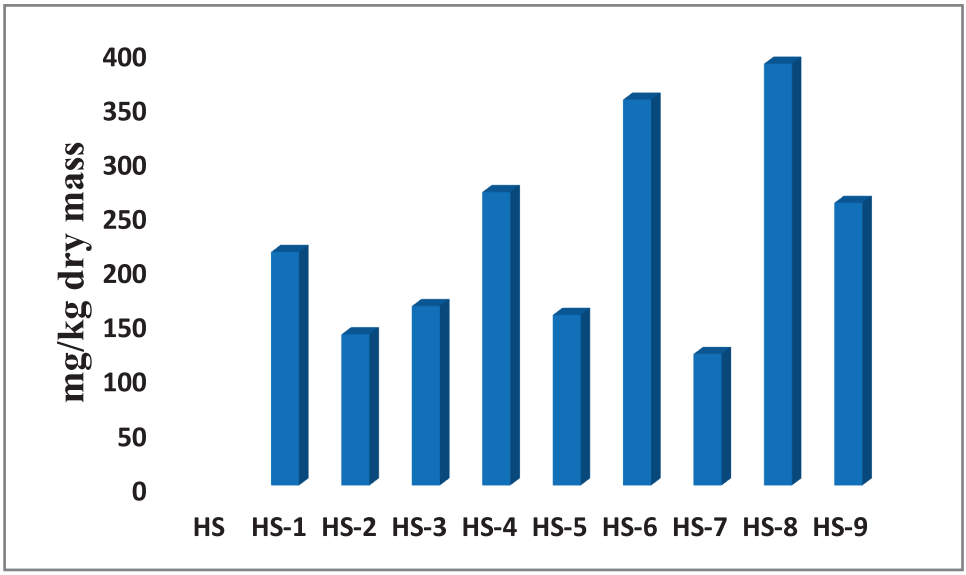

Figure 4. Zn concentration in sediment

L. in the period 2003-2004 from Beyşehir Lake (Tekin-Ozan, 2008).

Results reveal that the Zn concentration varies between tissues with the highest concentration in the liver followed by the gill and muscles. There are also changes in the Zn concentration in particular tissues in different seasons of the year. The Zn concentration in liver has significant fluctuations. It was determined 22.66 mg/kg and 14.11 mg/kg in the fall and winter of 2003 and 11.68 mg/kg and 12.73 mg/kg wet weight in the fall and winter of 2004. The concentration of Zn was 23.02 mg/kg and 23.41 mg/kg in the spring and summer of 2003 and respectively 16.63 mg/kg and 24.54 mg/kg wet weight in the spring and summer of 2004. Baharom and Ishak (2015) determined the Zn concentration in fish muscle of different species. The obtained results did not exceed the amounts of 0.33 mg/kg weight (wet weight). Compared to our study, the results are lower. Similar to our findings, Yi and Zhang (2012) reported an average Zn content of 7.55 mg/kg wet weight in *Pelteobagrus fulvidraco* (yellow-head catfish) muscle in the Yangtze River in China. Zn concentrations varied from 45.52 mg/kg to 86.08 mg/kg wet weight, according to Ismaniza and Idaliza's (2012) investigation of Zn in fish muscle of the species *Tilapia* sp. in Taman Mutiara Lake, Puchong, Malaysia. Although this quantity was over the permitted threshold (40 mg/kg) suggested by the FAO and Western Australian Food and Drink Regulations, it was still below the maximum allowable concentration (100 mg/kg) stipulated by the Malaysian Food Act (MFA, 1983; Baharom and Ishak, 2015).

High Zn concentration should be evaluated carefully as they can cause intoxication in people who consume fish with febrile, diarrheal symptoms, etc. (Chi et al., 2007). Numerous sources of Zn uptake are directly and/or indirectly related to the Vardar River basin. Except for location No. 8, where the concentration of Zn in the liver is

higher than the FAO limits (46.502 mg/kg wet weight compared to the limit of 40 mg/kg wet weight), it appears that the Zn concentration in the *S. cephalus* fish tissues is lower than the FAO limits. Zn concentrations in the liver are likewise high in HS-6 (39.791 mg/kg wet weight) and HS-4 (31.451 mg/kg wet weight), although these levels are within FAO and Western Australian Food and Drinking Regulations guidelines (FAO, 1983). According to data on Zn content in certain canned fish in America provided by authors, Ikem and Egiebor in 2005, two of the samples went beyond the FAO set. By calculating the weekly fish consumption and comparing it to the FAO's provisional tolerated weekly intakes (PTWI's) and acceptable daily intakes as standards for food additives and certain pollutants in foods, the authors highlight the need for caution when consuming fresh or canned fish (Ikem and Egiebor, 2005).

To determine the quantity of a chemical that may be used daily throughout a lifetime without posing a significant danger to one's health, the United States utilizes reference dosage, whereas the UK and the European Union have chosen tolerated daily intake (TDI). Zn in excess is bad for human health (ATSDR, 2004). Males and females (19-70 years old) and children (1-3 years old) have upper tolerated intake levels of Zn of 0.2 and 1.0 mg/day, respectively (Institute of medicine, 2003).

According to figure 4, the highest values of Zn concentration in sediment is in HS-8 and the lowest concentration was determined in HS-7 respectively 387.5 and 120.8 mg/kg dry mass. Regarding the amount of Zn in river sediment, several investigations have reported findings that are comparable to ours. According to Gale et al. (2004), the average Zn content in sediment dry mass ranged from 80 to 278 mg/kg in various American rivers. Zn concentrations in sediment from the Bebar River in Pahang, Malaysia varied from 9.833 mg/kg dry weight to 91.800 mg/kg dry weight, according to Shuhaimi-Othman et al. (2009). The effect of the year's dry and wet seasons on the Zn content in sediment was investigated by Duncan et al. (2018). The season in which the samples are collected and evaluated has an impact, according to the authors. They specifically examined 27 sediment samples from the Pra Basin of Ghana that were collected in various places. In the rainy season, the average concentration of Zn in the sediment at the 27 samples locations was only 35.622 mg/kg dry mass of sediment, compared to the dry season's 118.323 mg/kg dry mass of sediment. Edokpayi et al. (2016) conclude from their results on Zinc concentrations in water and sediment of the Mvudi River in South Africa that there are fluctuations in Zn concentrations in different months of the year, both in water and in sediment. Depending on the month of the year, the content of Zn in the sediment ranges from 14.481 to 39.88 mg/kg dry-weight sediment.

The high Zn concentration in the sediment of the Vardar River as well as *S. cephalus* fish liver in several locations along the river flow is related to the mining and processing industry of Zn in North Macedonia and the direct or indirect discharges into the Vardar River by significantly polluting the aquatic environment together with the organisms that live in it.

According to the statistical analysis, there appears to be a statistically confirmed association between the concentration of Zn in the sediment and the concentration of Zn in the liver ($P < 0.05$).

Conclusion

The Zn concentration in tissues (liver and muscles) differs in the 9 locations

where samples were obtained and analyzed. Zn concentrations are greater in the liver than in the muscles. The Zn concentration in one HS (HS-8), surpasses FAO regulations or limits. Zn concentrations in muscles are lower than FAO limits. According to the US EPA criteria, the Zn concentration in sediment in 9 places where samples were gathered for analyses, indicates a significant degree of Zn pollution. There appears to be a statistical relationship between Zn concentration in sediment and in liver. The Zn level found in sediment at each of the nine sampling locations reveals heavy pollution caused by industry or other activities conducted in these locations and needs more serious attention from authorities.

Acknowledgments

We would like to thank the Goce Delchev University-Stip, North Macedonia for providing the analyses by ICP-MS for this study.

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Zagađenje okoliša cinkom i rizik od njegovog unošenja u hranidbeni lanac

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Akumulacija cinka može se rabiti kao pouzdani biomarker za određivanje stupnja zagađenja okoliša u vodi, sedimentu i tkivima riječne ribe. U ovoj studiji, podatci dobiveni iz ICP-MS analize otkrili su da su razine cinka u sedimentu s 9 žarišnih točaka (*hotspots – HS*) bile: 214,5, 138,8, 164,8, 269,6, 156,6, 356,6, 120,8, 387,5, odnosno 259,7 mg/kg suhe mase sedimenta. Koncentracije cinka u jetri ribe *S. cephalus* na 9 žarišnih točaka bile su sljedeće: 11,623, 9,982, 13,514, 31,451, 27,513, 39,791, 10,034, 46,502 i 14,903 mg/kg mokre mase. Samo u žarišnoj točki HS-8 koncentracija cinka u jetri prelazi ograničenja Organizacije za hranu i poljoprivredu (FAO). Koncentracije cinka u mišićima varirale su od žarišne točke HS-1 do HS-9: 3,013; 7,021; 3,304; 6,513; 5,504; 2,802; 5,213; 6,342 i 8,704 mg/ kg mokre mase. Koncentracije cinka u mišićima nisu prelazile FAO smjernice i ne predstavljaju uzrok za zabrinutost za javno zdravlje. Čini se da postoji statistički odnos između koncentracije cinka u sedimentu i jetri. Razina cinka otkrivena u sedimentu na svakoj od devet lokacija uzorkovanja otkriva teško zagađenje prouzročeno industrijskim ili drugim aktivnostima koje se obavljaju na tim lokacijama i zahtijevaju veću pozornost vlasti.

Ključne riječi: *divlja riba, tkiva, Scualius cephalus, sediment, rijeka Vardar*