Content of Ni, Pb and Zn, in selected elements of ecosystem in three bays in the area of Sevastopol

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Abstract. The aim of the study was to evaluate the content of Ni, Pb and Zn in the water and larvae of fish of the genus *Atherinidae* L., caught in three bays in the area of Sevastopol. The study was conducted in 2012 in the three bays in the area of Sevastopol: Galubaya, Omega and Karantinna. The results indicate that the content of all elements studied was at a higher level than that observed in the uncontaminated basins. The average concentration of Ni, Pb and Zn in water was respectively: 1.199; 14.62 and 64.32 µg · dm^{-3}. The content of the elements studied in the examined fish larvae Atherinidae ranged from 6.413 to 19.65 mg Ni kg^{-1}, from 1.749 to 5.393 mg Pb kg^{-1} and from 97.16 to 215.24 mg Zn kg^{-1}.

1 Introduction

One of the major effects of human impact on the environment is the degradation of water resources in quantitative and qualitative terms. The degree and rate of degradation of the aquatic environment depend on the human impact, the time of exposure, the degree of transformation of the environment and the degree of environmental buffers. The assessment of environmental hazard resulting from human impact is made based on the inventory of the degrading factors and of the monitoring of the environment. Monitoring of pollution of water bodies is an important part of environmental and natural resources management policies. The use of living organisms in the assessment of the level of pollution of the aquatic environment is one of the most effective methods of environmental quality assessment [1]. The level of bioaccumulation of trace elements in living organisms allows evaluating the risk associated with their excess to the functioning of ecosystems and the safety of food produced in such environments [2,3] Aquatic ecosystems play an important role in the proper functioning of life on Earth. They participate in the global cycle of water, as well as of many elements, and play an important role in the primary production on Earth and binding of carbon from the atmosphere. They are breeding place of many environmentally and economically valuable animals and plants. Bodies of water are strategic parts of the economy of many countries. They provide opportunities for the development of water transport, tourism, aquaculture food sourcing, and waste disposal. The benefits that come from the exploitation of bodies of water often cause their unreasonable exploitation, leading to their degradation in quantitative and qualitative terms. The degree and rate of degradation of the aquatic environment depend on the level and duration of human impact, as well as the effectiveness of the compensatory treatments [4]. The larvae and juvenile fish specimens are becoming more widely used in bioindicative research [5,6] Despite the difficulties associated with obtaining the testing material, determining the accuracy of growth and development of fish larvae, as well as their trace element accumulation levels, allows a more complete interpretation of the toxicological effects of environmental pollution. Determining the possibility of successful breeding of animal species is an important parameter, which reveals their position in the changing environmental conditions. The most important indicators of the ecological condition of a body of water are: the number of fish, their health, growth and reproductive success level [7].

The aim of the study was to evaluate the content of Ni, Pb, Zn in the water and larvae of fish of the genus L. *Atherinidae*, caught in three bays in the area of Sevastopol. The second aim was to determine the level of bioaccumulation of these elements in the organisms used in the study.

2 Material and methods

The study was conducted in 2012 in the three bays in the area of Sevastopol: Galubaya, Omega and Karantinna. Fish larvae of the genus *Atherinidae* were caught in July 2012. The larvae were caught in the coastal shallows, at a depth of 1 m, using fishing nets. The collected material was transported to the laboratory immediately after

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collection, where it was preserved by drying. Before drying, the fish samples were washed thoroughly with distilled water. Fish larvae samples were subjected to wet digestion in a closed system with the use of microwave energy. The digestion was carried out using a microwave system Anton Paar Multivawe 3000. The biological material was dissolved in a mixture of HNO_3 and H_2O_2 at a ratio of 5: 1, v/v. The concentration of the analysed elements in the samples was determined using an atomic emission spectrometry with inductively coupled plasma in an apparatus Optima 7600 DV Perkin Elmer. The obtained results of mean element content were compared using the student's t-test, at the significance level of $p = 0.01$. Based on the results, calculated were the bioaccumulation factors of individual elements. The bioconcentration factor was calculated by dividing the concentration of the element in the dry matter of the larvae used in the experiment by the content of these elements in the water.

3 Results and discussion

The results of the study indicate significant differences in the content of soluble forms of the analysed elements in the water taken from each of the bays in the area of Sevastopol. The concentration of nickel in the water sampled from the Karantinna Bay was almost double compared to the water from the other bays. Lead content was also the highest in the water from the Karantinna Bay, twice as high in comparison with the water sampled from the Galubaya Bay (Table 1). Concentration of zinc in the tested water samples ranged from 51.42 to 85.67 mg µg Zn · dm^{-3} (Table 1). There were no statistically significant differences between the content of this element in the water in the Karantinna and Galubaya bays. The amount of this element found in the water from the Omega Bay was higher by more than half.

Table 1. The content of elements in water from bays [µg· dm^{-3}].

Points of sampling	Ni	Pb	Zn
Karantinna	4.653b	19.47c	55.86a
Omega	2.561a	14.24b	85.67b
Galubaya	2.383a	10.15a	51.42a
Detection limit	0.502	2.100	0.295

Oberholster et al [8] report the content of zinc in water from the lake Loskop in southern Africa in the range of 30 to 90 µg Zn · dm^{-3}. The concentration of nickel in the water of the river Ripol in Spain, impacted by anthropogenic pollution, was between 1.47 and 14.2 µg Ni · dm^{-3} [9]. Kahle and Zauke [10] report the content of zinc in the water from the Arctic Ocean at 0.3 µg Zn $dm^{-3,}$ which can be considered to be the natural content.

The use of fish larvae in this biomonitoring study was due to the fact that they are better indicators of changes in the quality of the environment in comparison to adult specimens, as pointed out by other authors [11,12].

Table 2. Statistical parameters of the results (mean, minimum value, maximum value mg·kg^{-1}).

	Ni	Pb	Zn	Ni	Pb	Zn	Ni	Pb	Zn
	Karantinnaya			Omega			Gałubaya		
mean	15.49b	3.425b	122.0a	9.96a	2.301a	176.9c	8.71a	3.109b	148.0b
min	11.02	2.606	97.16	6.410	1.749	138.2	7.302	2.231	137.9
max	19.65	5.393	146.8	13.58	3.187	215.2	11.94	3.879	160.3
SD	3.299	1.145	22.56	2.754	0.561	37.20	1.843	0.720	9.237
%*	21.29	33.44	18.48	27.65	24.40	21.02	21.17	23.15	6.241

Different letters at mean values indicate the statistically significant differences between the samples from each of the bays at p = 0.01.
* coefficient of variation

The level of nickel in the surveyed fish larvae of the genus L. *Atherinidae* ranged from 6.410 to 19.65 mg Ni · kg^{-1}. The concentration of this element in the larvae caught in the bays Karantinna and Omega did not differ significantly and was approx. 9 mg Ni · kg^{-1}. The accumulation of nickel in larvae from the Karantinna Bay was almost twice as high (Table 2). The differences in the nickel content in the larvae from the individual bays were similar to those found in water, and therefore the bioaccumulation factors of this element were at a similar level. The bioaccumulation factor of nickel ranged from 3329 to 3890. Similar quantitative relationships between elements content in the tested larvae were found in the case of lead. Its average amount in organisms caught in the Karantinna Bay was 3.425 mg Pb · kg^{-1} and was higher by approx. half as compared to the amount of this element in the larvae of the Omega Bay, in which 2.301 mg Pb · kg^{-1} was determined (Table 2). The average content of this element in the studied organisms from the Galubaya Bay was 3.109 mg Pb · kg^{-1} and did not differ statistically from the values of this parameter found in the case of the Karantinna Bay. The zinc content in the surveyed fish larvae ranged widely from 97.16 to 215.25 mg Zn kg^{-1}. Its largest accumulation was found in the organisms caught in the Omega Bay, and the larvae caught in the Karantinna Bay contained the least amount of the metal. The value of the bioaccumulation factor of zinc ranged from 2065 to 2878. The greatest value of this parameter was found in the larvae from the Galubaya Bay, and the lowest bioaccumulation of zinc was found in the larvae from the Omega Bay.

The research has indicated considerable accumulation variability of the analysed elements in the investigated fish larvae. The value of the relative standard deviation of the content of Ni, Pb and Zn in all the studied samples was accordingly: 34.64; 31.36 and 22.29%. The observed differences in the content of the analysed elements are not large, and are much smaller than reported in the literature. Many authors in this field draw attention to much greater differences in the concentrations of the analysed elements in fish from the same area, as compared to the results of their own research [13, 14, 15, 16]. The greatest content variability in the samples taken from the respective bays was observed in the case of lead. The relative standard content deviation of this element in the larvae from the bays Karantinna, Omega and Galubaya was respectively: 33.44; 24.40 and 23.15% (Table 2). Of all analysed elements, the lowest value of the coefficient of content variation was found in the Galubaya Bay. Among the surveyed areas, the least impact of human pressure on the quality of the environment is observed in the Galubaya Bay. This is due to a lower amount of pollutants discharged directly into the bay, and a greater coefficient of water exchange with the open sea [17]. In the bodies characterized by higher levels of human pressure, usually observed are greater differences in the content of trace elements in fish, as compared to the uncontaminated areas [13]. In our study, the content of elements is high and typical of contaminated environments. The content of lead per dry weight of several species of fish caught in several places in coastal areas in the southern part of China ranged from 0.02 to 0.8 mg · kg^{-1}, of zinc: from 4 to 13 mg kg^{-1}, and of nickel: from approx. 0.5 to approx. 1.5 mg kg^{-1} [14]. On the other hand, the concentration of nickel in various species of fish from the Yangtze River ranged from 0.07 to 6.35 mg kg^{-1} DM [18]. Leung et al. [16] reported concentrations of zinc, nickel and lead in several species of fish caught in the area of the Pearl River Delta in China at a similar level to that obtained in the present study. The authors emphasize that the researched area is characterized by a high level of pollution. Canli and Atli, [19] report lead content at 2.98 to 6.12 mg · kg^{-1}, and zinc at 16.48 to 37.39, in the muscles of fish caught in the Mediterranean Sea off the coast of Turkey, in areas with high human pressure. The bioaccumulation factor of the elements is an important indicator of the environment quality from the point of view of the threat of including them into trophic chains. In the present study, the bioaccumulation coefficient expressed as the ratio of the content of the element in the dry weight of fish larvae to that in water. The values of the bioaccumulation coefficients in the organisms used ranged from 400 to 3890 (Figure 1). The lowest value of this parameter was found in the case of lead, and the largest bioaccumulation factor was found for nickel. The mean value of the bioaccumulation factor of nickel 3624, of lead 214, and of zinc 2376. It was found that in relation to the literature data the significant differences in the values of this parameter in the larvae of fish from individual bays were low. The variation of the bioaccumulation factor of the studied elements ranged from approx. 7 to 35%. The bioaccumulation factor of Pb and Zn in the muscle of *Cyphocharax voga*, a freshwater bentos-feeding fish living in the River Sinos in Brazil in areas with different levels of human pressure was respectively: from 2514 to 9090 for zinc and 141 to 247 for lead. The values of the bioaccumulation factor of these elements in pelagic fish were usually several times smaller [20]. The authors found a significant negative correlation between the level of environmental pollution and the bioaccumulation factor of trace elements.

The values of the bioaccumulation factor of zinc in the muscles of several species of fish from the Danube in Serbia were, respectively, approx. 500 and 6000 [21].

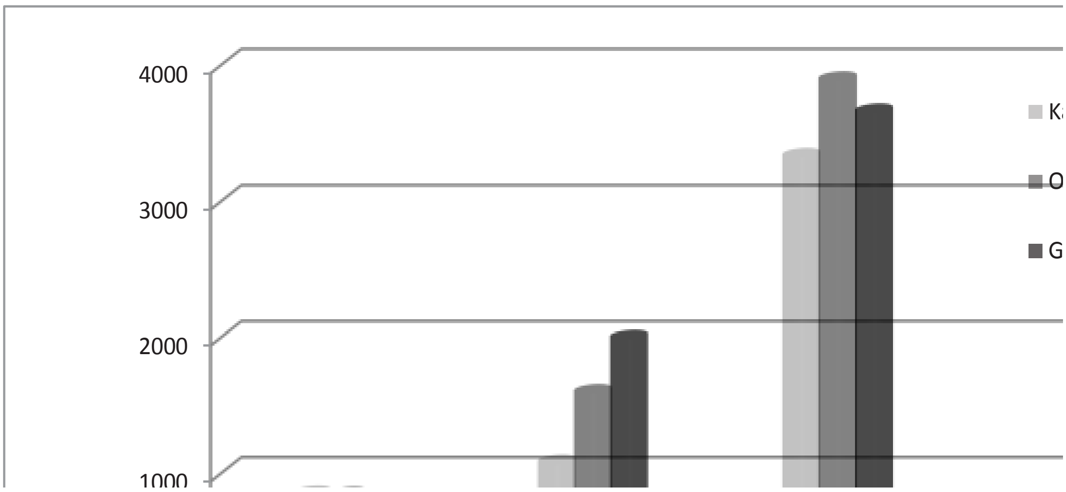

Figure 1. The bioaccumulation coefficient in the bodies of the larvae.

4 Conclusion

1. The largest nickel and lead content in the water were found in samples taken from the Karantinna Bay, and of lead, in the water sampled from the Omega Bay. The least amount of all the analysed elements was found in the Galubaya Bay.
2. The largest, nickel and lead content in the examined fish larvae were found in samples taken at the Karantinna Bay, and of lead, in organisms caught in the Omega Bay.

3. The concentration of the studied elements in water was, in sequence from the largest: Zn> Pb> Ni, while in the larvae of fish *Atherinidae L.*: Zn> Ni>Pb.
4. The value of the bioaccumulation coefficient of the analysed elements in *Atherinidae L.* fish larvae was, in sequence from the largest: Zn>Co>Pb.
5. The results of the study showed significant differences in the concentration of all elements in samples taken from the various bays, and large differences in the value of bioaccumulation factors.

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