

**Comparative Analysis of Heavy Metals (Mn, Zn, Ni, Co, Cr³⁺, Sr, Fe, Pb, Cd, Co)
Accumulation Ability in Fish Species *Sander lucioperca* L. and
Neogobius melanostomus P. at the Coastal Sea Waters of
The Northern and Central Part of Caspian Sea**

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Abstract: In the work there are described the biological indicators for the Northern and Central parts of Caspian Sea, i.e. *Sander lucioperca* L. and *Neogobius melanostomus* P. The purpose of the work is the research of the comparative bioaccumulation ability of one of the most toxic types of the salts of ten heavy metals types in various organs of the above mentioned species of fish. There were applied the methods of spectrophotometry with the usage of induced high-sensitive plasma and gas-liquid chromatography. It has been defined that the species *Sander lucioperca* L. and *Neogobius melanostomus* P. can be used in the described region as biological indicators with the purpose of general analytical estimation of the state of the environment pollution by salts of heavy metals.

Key words: Caspian Sea • Biological Indicators • Heavy metals

INTRODUCTION

The actual issue of the region is the comparative research of the accumulation level, migration and concentration of one of the most toxic types of heavy metals salts: Mn, Cr³⁺, Sr, Zn, Ni, Co, Fe, Pb, Cd, Co, that are following to the intensive anthropogenic activity, in the investigated zones of the Northern and Central parts of Caspian Sea. As a purpose of our studying, there have been chosen the widely-spread in the described studying region, species of fish - *Sander lucioperca* L. and *Neogobius melanostomus* P., the both species belong to one and the same family of perch-like fishes, they are widely spread and represent endemics in the studied points, they spawn and propagate, live actively, migrate to considerable distances, occupy similar ecological niches and habitats.

The widely-spread group of the pollutants is represented by associated with human activity (except Cr³⁺ and Sr) types of salts of heavy metals that have a toxic effect on living organisms. They are highly toxic and remain in basins for a long time. Most kinds of heavy metals represent complex inorganic compounds, the toxic impact of which can be caused by anion, or any other

physical-and-chemical quality of these elements; it should be noted that many kinds of heavy metals are contained in tissues and organs of living objects in natural background and take part in the processes of metabolism and life activity [1]. However, exceeding the values of the maximum permissible concentration of one or another kind of these elements can cause damage the vital functions of the organism and in some cases lead to fatal outcome.

The research of toxicity of heavy metals and its detailed analysis has been in the spotlight of many researchers for a long time and devoted to the description of the toxic impact of various metals on fish in quite broad area [2]. Most authors emphasize the high toxicity of different heavy metals, especially in the sweet water. Unfortunately, in many works there are given the concentrations of metals that cause the death of fish during a short term (1-3 hours), defined the toxicity of 10-20 concentrations of each kind of heavy metals (4-5 differences for each). The results gained by the author reliably show the existing toxicity of metals and, first of all, the high poisonous impact of heavy metals. As a result of the above-stated, the research of accumulation and migration of heavy metals was one of the foreground tasks in the given research.

The work had as its own purpose the performance of comparative analysis of the soil water sediment contamination factor ability and the spread in the Northern and Central Caspian Sea species of fish *Sander lucioperca* L. and *Neogobius melanostomus* P., to accumulate in various organs and tissues, one of the most toxic for living organisms, the above mentioned types of heavy metals that are associated with intensive anthropogenic activity and the possibility of usage the species *Sander lucioperca* L. and *Neogobius melanostomus* P., in monitoring of the investigated area as well.

MATERIALS AND METHODS

Sample Preparation: Several specimens of fishes *Sander lucioperca* L. and *Neogobius melanostomus* P. were caught in 4 points of sampling biological objects in the investigated place adjacent to Atyrau City in the Northern Caspian Sea region (47° 6'4.53"N, 51°54'48.99"E), (46°53'46.64"N, 51°38'12.96"E) and Aktau City (47° 6'4.53"N, 51°54'48.99"E), (43°37'0.77"N, 51°11'41.27"E) on the territory of the Central Caspian Sea, then they were delivered to the laboratory and studied with the usage of the method of morphometric analysis. The research was realized in summer period from July to August, 2011 – 2013. Then by turns there were taken organs and tissues (gills, reproductive organs and muscle tissue) out of the caught specimens of fish. Each organ was weighed from 1 to 5 g and then prepared for the further analysis. As a control group there were taken the identical species of fish contained in aquarium in pure running water without any polluting elements and admixtures.

Sample Extraction and Analysis

Heavy Metals Extractions: Fish organs samples, gills, gonads and muscle tissue were collected and individually air-dried at room temperature of 21°C to reduce the moisture content. The fish samples were left to reduce the moisture content for ten (10) days. Then the samples were homogenized, with a ceramic mortar and pestle and passed through a sieve for particle size reduction.

Since sample results are to be calculated on a dry weight basis, a portion of sample was weighed at the same time as the portion used for analytical determination.

This portion was dried in an oven at temperature of 115°C then allowed to cool in a desiccator before weighing.

Approximately 0.5g of dried fish sample organ was weighed using an analytical balance and transferred into Teflon microwave bottles/containers. 20ml of

concentrated nitric acid (HNO₃) was added to the bottles in a fume hood. The bottles were properly sealed, placed in a vessel and put in the microwave apparatus according to manufacturer's instruction. The temperature of each sample in the microwave rose to 175°C in approximately 5 minutes and remained at same temperature for the remaining 5 minutes. At the end of the microwave program, the vessel was left to cool to room temperature before removal from the microwave. After removal from the microwave, the bottles were left to cool more for another 2 hours before carefully uncapping in the ventilated fume hood. When it was sufficiently cool, the organ samples were transferred in acid clean volumetric flasks.

However, the digested samples contained some particulates. The digested samples were put in centrifuge bottles and placed in Eppendorf centrifuge 5702 for 15 minutes at 4.5rpm. The supernatant was sufficiently cleared, filtered with Whatman 42 filter paper and transferred into a 50ml volumetric flask and the digest was diluted to the total volume of 50 ml [3].

ICP-OES Analysis: A thermos model ICP-OES was used for triplicate reading of each blank sample, mixed metal standard, nitric acid solution and a fish organs sample extract. The instrument was calibrated and profiled using the mixed calibration standard solution. The system was rinsed for one minute with the deionized water before the analysis of each sample.

Statistical Analysis: Statistical differences between particular organs of *Sander lucioperca* L. and *Neogobius melanostomus* P., with respect to mean concentrations of elements were evaluated by ANOVA on log-transformed data to obtain a normal distribution of features. Normality of analyzed features was checked by Shapiro-Wilk's test and the homogeneity of variances by Bartlett's test. Statistical confidence was set at $p = 0.05$. Fish's ability to take up the elements from its environment and translocation rate of the elements within the fish were, evaluated by the Index Bioaccumulation or Translocation Factor (TF), expressed by the following ratios: metal concentration in gills/metal concentration in muscles and metal concentration in gonads. All statistical calculations were carried out in using following program [4].

RESULTS

Concentration of Heavy Metals in the Tested Objects: The results of analysis of the laboratory research on detection of heavy metals concentration, revealing the

ranges of concentrations of elements in the water and sediments from the examined ponds as well as in different organs of *Sander lucioperca* L. and *Neogobius melanostomus* P., are shown in (Tables 1 and 2).

Transfer factor (TF) was calculated only for those elements, which were detected in the all fish organs. On average, transport efficiency from sediment into the fish organs was higher than this within the fish itself. The bioaccumulation factor for all the metals analyzed in gonads of *Sander lucioperca* L. and *Neogobius melanostomus* P., (gonads/water sediment ratio) was estimated to exceed 1 confirming an intensive gonads uptake of the most studied metals in the having species. The highest gonads/water sediment ratio was noted for Sr while the lowest value was calculated for Cd. Translocation factors for all the elements analyzed in *Sander lucioperca* L. and *Neogobius melanostomus* P., were significantly below 1 confirming high gonads retention capacity in respect of the studied elements and low intensity of their transfer to other fish's organs. Mobility of the metals analyzed within the fish varied in different parts of an organism. The translocation rate of all

the elements studied in Atyrau and Aktau groups, between the gills, muscle tissue and gonads as well as to compare, between the same control groups of fish organs: gills, muscle tissue and gonads, showed comparatively low concentration of all studied metals, not exceeding MPC and experimental groups of fish.

The following statistical relationships, expressed by Pearson's correlation ($p < 0.05$), between chemical composition of the marine's fish environment and concentrations of the studied elements in the fish were calculated in this study.

According from (Table 2) it is seen that the greatest ability to accumulation in species *Neogobius melanostomus* P. was shown by the element Sr; the concentration of this element in the organs is high and exceeds MPC from 200 to 300 times comparing both with the control group of the organisms and the Atyrau population. At (Table 2) there is indicated that concentration of Sr is considerably higher than MPC in species that closely contact with the bottom of the sea, for example in fish *Neogobius melanostomus* P. There is also shown the exceeding of the element Cr^{3+} in the

Table 1: The main concentration of heavy metals in organs of *Sander lucioperca* L., Atyrau, Northern Caspian sea

	Gills	Control	Muscles	Control	Gonads	Control
Pb	1.77±0.88	^b ND	1.80±0.11	1.18±0.59	4.50±2.25	1.18±0.59
Excess, MPC	5.70±2.84	^b ND	5.80±2.9	3.80±1.9	14.51±7.25	3.80±1.9
MPC 0.31	MPC 0.31	MPC 0.31	MPC 0.31	MPC 0.31	MPC 0.31	MPC 0.31
Cu	0.10±0.6	0.03±0.01	0.56±0.28	0.15±0.075	0.85±0.42	0.70±0.34
Excess, MPC	0.02±0.1	0.06±0.04	0.11±0.05	0.03±0.010	0.17±0.060	0.14±0.09
MPC 5.0	MPC 5.0	MPC 5.0	MPC 5.0	MPC 5.0	MPC 5.0	MPC 5.0
Cd	0.16±0.07	0.02±0.01	0.08±0.04	^b ND	0.10±0.05	^b ND
Excess, MPC	1.60±0.9	0.20±0.3	0.80±0.5	^b ND	1.00±0.5	^b ND
MPC 0.1	MPC 0.1	MPC 0.1	MPC 0.1	MPC 0.1	MPC 0.1	MPC 0.1
Zn	32.56±16.28	12.01±4.9	22.20±11.1	5.90±2.95	70±38	17.76±8.92
Excess, MPC	6.51±3.22	2.4±1.2	4.44±2.20	1.18±0.57	14±8	3.55±1.77
MPC 5	MPC 5	MPC 5	MPC 5	MPC 5	MPC 5	MPC 5
Fe	82.68±41.3	22.23±11.1	103.2±51.5	6.84±3.42	111.15±55.7	60.84±30.43
Excess, MPC	1.65±0.91	0.44±0.19	20.60±10.3	0.14±0.6	2.22±1.10	1.21±0.60
MPC 50	MPC 50	MPC 50	MPC 50	MPC 50	MPC 50	MPC 50
Ni	6.72±3.36	1.00±0.55	7.04±3.5	0.75±0.37	8.96±4.48	0.50±0.29
Excess, MPC	13.44±6.72	2.00±1.85	14.00±8.0	1.50±0.75	17.90±8.95	1.03±0.7
MPC 0.5	MPC 0.5	MPC 0.5	MPC 0.5	MPC 0.5	MPC 0.5	MPC 0.5
Co	0.30±0.15	^b ND	0.80±0.45	0.60±0.3	0.70±0.35	^b ND
Excess, MPC	0.06±0.03	^b ND	0.16±0.08	0.12±0.6	0.14±0.7	^b ND
MPC 0.5	MPC 0.5	MPC 0.5	MPC 0.5	MPC 0.5	MPC 0.5	MPC 0.5
Mn	5.20±2.6	3.12±1.56	2.60±1.3	1.30±0.65	1.80±0.9	^b ND
Excess, MPC	26.04±13	15.60±7.8	13.01±6.4	6.50±3.27	9±5.7	^b ND
MPC 0.2	MPC 0.2	MPC 0.2	MPC 0.2	MPC 0.2	MPC 0.2	MPC 0.2
Sr	13.50±6.75	0.50±0.29	9.45±4.72	0.52±0.26	5.40±2.7	0.52±0.26
Excess, MPC	1.92±0.96	0.07±0.035	1.35±0.67	0.07±0.031	0.77±0.38	0.07±0.031
MPC 7.0	MPC 7.0	MPC 7.0	MPC 7.0	MPC 7.0	MPC 7.0	MPC 7.0
Cr(3+)	0.95±0.48	0.19±0.094	0.86±0.43	0.24±0.12	1.03±0.53	0.44±0.19
Excess, MPC	0.16±0.08	0.03±0.015	0.14±0.07	0.04±0.01	0.17±0.08	0.07±0.03
MPC 6.0	MPC 6.0	MPC 6.0	MPC 6.0	MPC 6.0	MPC 6.0	MPC 6.0

MPC - Maximum permissible concentration

^amg/kg. ^bND - no detection level

Table 2: The main concentration of heavy metals in organs of *Neogobius melanostomus* P., Aktau, Central Caspian sea

	Gills	Control	Muscles	Control	Gonads	Control
Pb	17.4±8.7	0.66±0.24	17.4±8.7	1.32±0.66	5.8±2.9	0.66±0.24
Excess, MPC	56.1±27.4	2.12±1.10	56.1±27.4	4.25±2.12	18.7±9.35	2.12±1.10
MPC 0.31	MPC 0.31	MPC 0.31	MPC 0.31	MPC 0.31	MPC 0.31	MPC 0.31
Cu	0.78±0.39	0.3±0.01	0.26±0.9	1.2±0.6	1.04±0.52	0.9±0.3
Excess, MPC	0.15±0.81	0.06±0.02	0.05±0.025	0.24±0.12	0.2±0.1	0.18±0.06
MPC 5.0	MPC 5.0	MPC 5.0	MPC 5.0	MPC 5.0	MPC 5.0	MPC 5.0
Cd	0.14±0.07	0.02±0.01	0.2±0.1	0.08±0.03	0.02±0.01	0.02±0.01
Excess, MPC	1.4±0.4	0.2±0.1	0.6±0.3	0.8±0.4	0.2±0.1	0.2±0.1
MPC 0.1	MPC 0.1	MPC 0.1	MPC 0.1	MPC 0.1	MPC 0.1	MPC 0.1
Zn	4.62±2.31	10.36±5.18	16.5±2.83	4.01±1.07	20.46±2.33	14.06±7.03
Excess, MPC	0.92±0.46	2.07±1.036	3.3±1.65	13.91±1.95	4.09±0.08	2.81±0.94
MPC 5	MPC 5	MPC 5	MPC 5	MPC 5	MPC 5	MPC 5
Fe	35.2±17.6	11.62±3.15	9.96±4.98	9.16±4.58	46.48±15.2	39.21±18.5
Excess, MPC	0.7±0.2	0.23±0.5	0.19±0.09	0.18±0.06	0.92±0.46	0.78±0.06
MPC 50	MPC 50	MPC 50	MPC 50	MPC 50	MPC 50	MPC 50
Ni	5.32±1.67	3.04±1.52	4.8±0.8	4.56±0.52	3.04±0.05	2.88±1.45
Excess, MPC	10.64±5.32	6.08±1.05	9.6±2.4	9.12±4.56	6.08±3.04	5.76±1.64
MPC 0.5	MPC 0.5	MPC 0.5	MPC 0.5	MPC 0.5	MPC 0.5	MPC 0.5
Co	0.2±0.1	1±0.04	0.4±0.2	0.5±0.2	0.1±0.1	^b ND
Excess, MPC	0.04±0.02	0.2±0.1	0.08±0.03	0.1±0.1	0.02±0.01	^b ND
MPC 5	MPC 5	MPC 5	MPC 5	MPC 5	MPC 5	MPC 5
Mn	21.42±5.11	3.7±1.85	35.7±12.80	7.4±2.4	7.14±2.38	2.96±0.98
Excess, MPC	107.1±23.55	18.5±7.25	178.5±59.5	37±12.3	35.7±11.9	14.8±4.9
MPC 0.2	MPC 0.2	MPC 0.2	MPC 0.2	MPC 0.2	MPC 0.2	MPC 0.2
Sr	172.8±47.6	1.98±0.66	295.68±88.56	6.6±1.65	268.8±134.4	3.3±0.82
Excess, MPC	24.68±8.22	0.28±0.09	42.24±14.08	0.94±0.31	38.4±19.2	0.47±0.15
MPC 7.0	MPC 7.0	MPC 7.0	MPC 7.0	MPC 7.0	MPC 7.0	MPC 7.0
Cr(3+)	6.12±2.04	4.21±1.40	6.11±3.05	4.77±1.59	3.06±1.02	1.03±0.34
Excess, MPC	1.02±0.51	0.7±0.04	1.01±0.49	0.79±0.26	0.51±0.17	0.17±0.05
MPC 6.0	MPC 6.0	MPC 6.0	MPC 6.0	MPC 6.0	MPC 6.0	MPC 6.0

MPC - Maximum permissible concentration

^amg/kg ^bND - no detection level.

organs of the species *Neogobius melanostomus* P., unlike *Sander lucioperca* L. The degrees of toxicity of hexa- and trivalent chromium are considerably different.

It is probable that such results are connected with sedimentation and storing up of radionuclides on the bottom and coastal soil whence they get into the water and with the food into the organisms of the above species, because the coastal water area of Aktau City places a number of plants of atomic industry.

According to the results of the analysis there was detected the ability of the species *Sander lucioperca* L and *Neogobius melanostomus* P., to store up in their organisms such studied metals as lead (Pb), manganese (Mn), nickel (Ni) and zinc (Zn).

In the species *Sander lucioperca* L., sampled near Atyrau City the exceeding of Pb in organs varies from 3.80 mg/kg to 14.51 mg/kg, Mn from 9 mg/kg to 26 mg/kg. Comparative analysis of Zn and Ni concentration showed the exceeding in the organs of species *Sander lucioperca*

L. Zn from 4.44 mg/kg to 14 mg/kg. The content Ni at the *Sander lucioperca* L., is from 13.44 mg/kg, to 17.9 mg/kg, in comparison with the type *Neogobius melanostomus* P. of the Aktau group.

The content Pb, in the control group, in comparison with the Atyrau group makes from 0 mg/kg, to 5.80 mg/kg, Mn from 2 mg/kg, to 15.6 mg/kg., Zn from 3.55 mg/kg to 9.10 mg/kg., Ni from 1 mg/kg, to 2 mg/kg.

At the specie *Neogobius melanostomus* P. to be concern on the Aktau group, the excess of identical elements in bodies, is characterized by the considerable share of the content Pb from 18.7 mg/kg to 56.1 mg/kg, Mn from 35.7 mg/kg to 178.5 mg/kg, Ni from 6.08 mg/kg to 10.64 mg/kg, Zn from 0.92 mg/kg to 4.9 mg/kg in comparison with the Atyrau group.

The content of Pb, in the control group, in comparison with Aktau group makes from 2.12 mg/kg, to 4.25 mg/kg, Mn from 14.8 mg/kg, to 37 mg/kg., Zn from 2.72 mg/kg to 13.91 mg/kg., Ni from 5.76 mg/kg, to 9.12 mg/kg.

Out of presentation of high toxicity and long bioaccumulation in fabrics of the living organisms, some metals are microcells to be necessary for metabolic processes, but in high density they cause a poisoning. Others Lead (Pb), in the normal, are not met in an organism and consequently, theoretically, they can be toxic in any concentration. Toxicity of Lead (Pb) is slightly lower than toxicity of copper and cadmium, (Cu and Cd) however it is high enough and in concentration from 0.1 - 0.4 mg \l Pb, it is obviously harmful for many kinds of fish.

It is known that toxicity of Zinc (Zn) is close to toxicity of lead (Pb). The data shows that on degree of harm, metals represent the rather diverse group. For example, strontium (Sr) is least toxic for fish and can be joined with the group of less toxic metals Mn and Co (manganese and cobalt). Copper, lead, cadmium, zinc, nickel (Cu, Pb, Cd, Zn, Ni) and trivalent chrome (Cr^{3+}) are highly toxic for fish. Salts of metals some of this group are extremely toxic for fish, showing their action even at the concentration from 0.02-0.004 mg\l. Cadmium (Cd) is a little less toxic and it has damaging influence at the metal concentration from 0.1-0.5 mg\l.

Apparently from the following data, Iron (Fe) shows the greatest ability to accumulate 141.842 mg/kg for test objects from Atyrau zone, as shows the second site of the research zone in Aktau city, accumulation ability 46.48 mg/kg, the level of the content and excess of the given element remains at the low level in bodies. The content of Fe, in control groups, remains at the rather low level and actually, does not exceed the maximum concentration limit that is similar to types *Sander lucioperca L.* and *Neogobius melanostomus P.* (Table 1, Table 2).

It is necessary to notice that on the toxicity degree iron (Fe) does not represent so high danger both for hydrocoles and for a human being, the maximum concentration limit of Fe is 50 mg \kg, in comparison with zinc, manganese and lead (Zn, Mn, Pb). It is well-known that in an organism of animals iron (Fe) is a part of set of enzymes which participate in oxidation-reduction reactions, mainly in the course of breath. So the high concentration of iron as well as other salts of heavy metals, is quite predicted and also thanks to the in the leading content of ions of iron in stratum waters arriving to the Caspian sea at oil extracting. Higher concentration of the given metal in organisms collected from bottom sites, are explained by fast transition of dissolved ionic forms Fe (II) and Fe (III) into a deposit in the form of various complexes with organic substances.

Also it's seems to know the sequence of metal concentration decreasing in the following order in the organs of the studied fishes, *Sander lucioperca L.* Fe showed the highest concentrations in gonads and also Zn in reproductive part, (Table1). Mn was mainly accumulated in the gills and muscle tissue, whereas Ni either in the reproductive, muscles and gills of the studied fish (Table 1).

Whereas sequence of metal concentration decreased in the following order in the organs of the studied fishes *Neogobius melanostomus P.* Sr showed the highest concentrations in the muscle and reproductive tissue. Pb shows similar accumulation concentration at gills and muscle tissue, (Table 2). Mn was mainly accumulated in the muscle tissue, whereas Fe in reproductive tissue (gonads) and gills of the studied fish, (Table 2). Zn also showed high accumulation in reproductive tissue (gonads), but low accumulation in gills, whereas Ni, mainly accumulated in all organs, Cr^{3+} showed high concentration in same organs gills and muscles.

DISCUSSION

The mean concentrations of majority of the heavy metals in different organs of *Sander Lucioperca L.* and *Neogobius Melanostomus P.*, (Tables 1 & 2) were found to be relatively low and within the ranges of the geochemical background values [5]. Nonetheless, the content of the following elements: Mn, Zn, Ni, Pb and Sr were high in muscles and gills of the studied fish. Other organs of both species of the fish were also high in Pb, Mn, Zn and Sr. Toxic concentration of Mn was found in gills, while Pb exceeded toxicity threshold in the gonads. Nonetheless, transfer of some elements from the water sediments into the fish organs tissues appeared to be supply dependent. Statistically significant correlations which were noted between concentrations of the following metals: Zn, Mn, Pb, Ni and Sr in the water sediments and their content in the below organs of *Sander lucioperca L.* and *Neogobius melanostomus P.*, suggested that water sediments may be the main pollution source of these elements for the fish organism. This supports findings, that postulated that the elements taken during the life inhabitant of the fish were mainly became from water sediment derived [6].

Mn is another essential microelement for fishes being involved in enzyme activity. Water, however seems to be a meaningful source of Mn element for *Sander lucioperca L.* and *Neogobius melanostomus P.*, fish species, as

significant correlation between the content of Mn in the water sediments and the sampled fish was noted in this study. As far as Ni is concerned, significant, positive correlations between content of this element in the water sediments and its concentration in the gills, muscles and reproductive organs (gonads). Both high content of Mn in the gills and muscles of *Sander lucioperca* L. and *Neogobius melanostomus* P., representing the highest value compared to the other calculated in this study, suggest availability of this metal to fishes from the water sediments and noticeable ability of fish for its uptake and accumulation. The results for *Sander Lucioperca* L. and *Neogobius melanostomus* P., studied herein have also revealed highest Mn concentration in the *Neogobius melanostomus* P fish species as well. Nonetheless, the highest content of Mn was found in the gills and muscles tissue of *Neogobius melanostomus* P fish species. The Mn content in gills and muscle tissue of *Neogobius melanostomus* P. was estimated to be 75% lower than in gills and muscle tissue of *Sander lucioperca* L. specie. Accumulative factor for the gills and muscle tissue was much higher than that for the reproductive organs (gonads) in both studying species. Manganese showed linearly correlated concentrations in the water sediments and gills, muscle tissues, suggesting potential use of this organs of in bio indication of trace elements ($r = 0.75$; $p < 0.05$).

Iron (Fe) is vital for the fish development playing a key role in processes of energy transformations needed for synthesis and other life process of the cells. The analysis carried out herein showed that Fe has been accumulated in muscle and gonads of both species to the highest extent. Concentration of this element in the *Sander lucioperca* L. and *Neogobius melanostomus* P., organs was estimated to be higher than values for both species from unpolluted water areas [7]. The TF values for iron were estimated to be very low supporting findings, which are reported slow translocation of Fe within fish's body and its tendency to accumulate in their inner organs [8].

Zinc is an essential element for many organisms growth being actively taken up by the living organisms during their lifecycle. High gonads/gills/muscles ratio and the highest concentration of Zn in abovementioned organs, of the studied fish revealed that Zn was easily taken up by the *Sander lucioperca* L., in compare to *Neogobius melanostomus* P. It is likely that the reproductive organs acted as some kind of absorption point, because Zn concentration in gonads was increased

by 42.7% compared to gills and muscles. Zinc mobility within the fish tissues is low and therefore its translocation ability in the studied organs is reduced. Therefore *Sander lucioperca* L., can be considered as gonads accumulator with regard to Zn, likewise *Neogobius melanostomus* P., where concentration of Zn, also revealed in higher concentrations, but in lower proportion. Zinc showed significant correlations between the concentration values in the gills and muscles ($r = 0.97$; $p < 0.05$) as well as gonads ($r = 0.71$; $p < 0.05$), therefore reproductive organs (gonads) of studied fishes can be used as bio indicator of environmental contamination.

Copper is an essential element for many fish species growth and occurs in enzymes of oxidation–reduction reactions. In the present research, the non-highest concentration of Cu was noted again in *Sander lucioperca* L. and *Neogobius melanostomus* P., species gonads, which have appeared as some kind of accumulative center, for preventing translocation of Cu and many other studied heavy metals types, into the reproductive organs of both fish species. The previous findings corresponded that Cu has relatively low mobility and being accumulated mainly in reproductive organs [8]. In the present research *Sander lucioperca* L., values for Cu (Table 1) were quite similar accumulation of this metal compared to the *Neogobius melanostomus* P., presented in the (Table 2), indicating relatively similar mobility of Cu within organs tissue in both mentioned fish species. Copper is a vital microelement for many aquatic organisms and its mobility observed in this study can be explained by its active transport to fish organs. The content of Cu in the water samples was correlated with its concentration in the organs ($r = 0.84$; $p < 0.05$) therefore gonads of both species, can be used in bio indication of Cu pollution in the environment.

Cadmium is a highly toxic and non-essential element effecting growth, metabolism as well [9]. Results of this study show that gills of *Sander lucioperca* L. and *Neogobius melanostomus* P., can accumulate more higher amounts of Cd, proportionally to its concentrations in the muscle and reproductive tissues (significant, positive correlation between the content of Cd in the muscles, gonads and the fish's gills) ($r = 0.72$; $p < 0.05$). The content of Cd in the water sediments was about to 27.4% and its concentration was below the detection threshold.

The concentrations of **Pb**, noted in *Sander lucioperca* L., organs decreasing in the following order: gonads - muscles - gills, but in second fish organs *Neogobius melanostomus* P., the contamination of Pb

revealed the same concentration in muscles and gills tissues, (Table 2), with the lowest concentrations found in gonads (gills-muscles-gonads). This scheme of Pb accumulation could be linked to its intensive mobility, pretty similar to mobility of Mn, Zn, Ni and Sr, apparently affecting its transport rate within the main fish organs. Lead showed linearly correlated concentrations in water sediment and abovementioned organs suggesting potential use these organs of *Sander lucioperca* L. and *Neogobius melanostomus* P., as a bio indicator of environmental contamination by metals ($r = 0.57$; $p < 0.05$).

The mobility of Ni in studied fish species varies from being mobile in some aquatic organisms to immobile in other water species. In this research, Ni showed similar mobile activity in both organisms *Sander lucioperca* L. and *Neogobius melanostomus* P., showing a lower value in all studied organs of *Neogobius melanostomus* P. (Table 2). Similar results have been obtained by other investigators [10]. The concentration of Ni in sea water sediments of the examined reservoir also was positively correlated with its concentration in organs ($r = 0.63$; $p < 0.05$). The observed relation suggests a possibility of using these organs of *Sander lucioperca* L. and *Neogobius melanostomus* P., in bio indication process.

Regarding Co and its biochemical function, it is not clear whether Co is essential for many water living organisms, including two studied fish species, although there are some evidences of a favorable effect of this metal on fish growth. In this research, the maximum quantity of this element concentration was found in muscles, reproductive tissues and gills of *Sander lucioperca* L. and it's very low concentration value in all organs of *Neogobius melanostomus* P. The reason for the high accumulation rate in the muscles could be its big immobilization ability in the research area of Northern Caspian Sea in compare to Central parts of the Sea. Cobalt is also easily taken up by the aquatic organisms through the epithelium tissue and can further absorb in internal organs, including reproductive part. This seems to be confirmed by the statistically significant correlation between the content of Co in the sea water sediments and its concentration in the muscle tissue in this study ($r = 0.76$; $p < 0.05$). Other significant correlations found between the content of Co in the sea water and reproductive organs ($r = 0.70$; $p < 0.05$) and gills ($r = 0.55$; $p < 0.05$) suggest potential use of *Sander lucioperca* L. and *Neogobius melanostomus* P., organs in environmental bio indication of Co contamination.

Chromium 3+ (Cr^{3+}), is an element regarded as toxic and mutagenic chemical element for many living organisms. In contamination of Chromium³⁺ in studied organs of *Neogobius melanostomus* P., were found to contain high amounts of Cr^{3+} , in significantly higher proportions than in *Sander lucioperca* L., from point of Central Caspian sea waters. Similar high concentrations of Cr^{3+} in gills and muscles tissues (Table 2) as well as high sea water sediment ratio suggest that *Neogobius melanostomus* P., can be considered a mostly external bodies accumulator for Cr^{3+} . The analysis also revealed that Cr^{3+} was accumulated predominantly in the reproductive organs of *Sander lucioperca* L., in compare to previous fish species and the metal content decreased according to the following pattern: gonads, gills and muscle tissues.

Strontium is one of the radioactively chemical elements as well. Strontium - a component of micro-organisms, plants and animals. In marine radiolarians (acantharians) skeleton is composed of strontium sulfate - celestite. Algae contain 26-140 mg strontium per 100 g of dry matter, terrestrial plants - 2.6, marine animals - 2-50, terrestrial animals - 1.4, bacteria - 0.27-30. Accumulation Strontium various organisms depends not only on its type, characteristics, but the ratio among strontium with other elements, mainly Ca and P, as well as the adaptation of the organisms to certain geochemical environment. Animals get Strontium from food and water. Strontium is absorbed with thin and allocated mainly the large intestine. A number of substances (polysaccharides algae, cation exchange resins) prevent the absorption of strontium. As a result of accumulation ability Sr showed the highest concentration in muscle tissue and reproductive organs and the lower percent in gills in *Neogobius melanostomus* P., fish species, the accumulation result in organs of *Sander lucioperca* L., showed completely different picture, concentration of Sr in compare to previous unit, presented lowest concentration in all studied organs, in following proportions: gills - muscle tissue – gonads, in compare to *Neogobius melanostomus* P.

CONCLUSION

The received results allow making the following conclusions:

From the resulted complex analysis of accumulation and migration of salts of heavy metals in fabrics of sorts *Sander lucioperca* L., it is possible make up the degree of

sequence of accumulation of the given elements: Fe> Zn> Mn> Ni> Pb> Cr³⁺> Co> Sr> Cu> Cd and *Neogobius melanostomus* P., Sr> Pb> Mn> Fe> Zn> Ni> Cr³⁺> Cu> Cd> Co.

There was revealed excess, as a whole, of elements Mn, Pb, Zn, Ni, Fe, Sr, Cr 3 + from ten investigated metals. The content of Fe, Zn, Pb and Ni exceeds the maximum concentration limit in 70% of the investigated test objects and the content of Cu, Co and Cd is less than at 50%. Fe shows the greatest accumulative activity (on the average of 82.68 up to 111.15 mg/kg), mostly in *Sander lucioperca* L., organs and highest accumulative activity of strontium Sr (on the average of 172.8 up to 295.68 mg/kg), in *Neogobius melanostomus* P., organs.

The significant, positive correlations found between the content of Mn, Zn, Pb, Ni, Cr³⁺, Sr in the studied environment and the levels of these elements in the organs of these fishes indicate the potential use of *Sander lucioperca* L. and *Neogobius melanostomus* P in biomonitoring of environmental contamination with these metals.

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REFERENCES

1. Al-Mohanna, M.M., 1994. Residues of some heavy metals in fishes collected from (Red Sea Coast) Jisan, Saudi Arabia, J. Environ. Biol., 15: 149-157.
2. Vardanyan, L.G. and B.S. Ingole, 2006. Studies on heavy metal accumulation in aquatic organisms from Sevan (Armenia) and Carambolim (India) lake systems. Environ. Int., 32: 208-218.
3. Canli, M. and G. Atli, 2003. The relationships between heavy metal (Cd, Cr, Cu, Fe, Pb, Zn) levels and the size of six Mediterranean fish species, Environ. Pollut., 121: 129-136.
4. STATISTICA (Data Analysis Software System), Version 9.0. www.statsoft.com
5. Kabata-Pendias, A., B.A. Manny and A.B. Mukherjee, 2007. Heavy metals in aquatic macrophytes drifting in a large river. Hydrobiologia, 219: 333-344.
6. Ray, S., D.W. McLeese and M.R. Peterson, 1981. Accumulation of copper, zinc, cadmium and lead from two contaminated sediments by three marine invertebrates. A laboratory study//Bull. Environ. Contam. Toxicol. V, 26.(5): 315-322.
7. Szymanowska, A., A. Samecka-Cymerman and A.J. Kempers, 1999. Heavy Metals in Three Lakes in West Poland. Ecotoxicol. Environ. Safe., 43: 21-29.
8. Demirezen, D. and A. Aksoy, 2004. Bioaccumulation, detection and analyses of heavy metal pollution in sultan marsh and its environment. Water Air Soil Pollution, 164: 241-255.
9. Divan, A.M., de P.L. Oliveira, C.T. Perry, V.L. Atz, L.N. Azzarini-Rostirola and M.T. Raya-Rodriguez, 2009. Using wild species as indicators for accumulation of emissions from thermal power plant, Candiota, South Brazil. Ecol. Indic., 9: 1156-1162.
10. Bonanno, G. and R.L. Giudice, 2010. Heavy metal bioaccumulation by the organs of *Phragmites australis* (common reed) and their potential use as contamination indicators. Ecol. Indic., 10: 639-645.