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Research Article

Evaluation of the Influence of Heavy Metals Contamination in Abiotic and Biotic Environments of the Lower Reaches of Kura River

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Abstract: Waters of Kura River are main sources for drinking water in Azerbaijan. Therefore, any decrease of quality of water creates danger for environmental protection issues of the whole region. Heavy metals (HM) are one of the main pollutants of the water. Diluted and highly-dispersed forms of HMs forming various complexes with the components of natural environment, then can be transferred by the water flows as well as they can be accumulated in the bottom sediments (BS) and water organisms. For efficient assessment of ecological state of the environment, it is necessary to have sustainable control of HMs content in all links of the following chain: abiotic environment (water, bottom sediment) - biotic environment (benthophage, plankton, phytophages euryphage predator). Present study is devoted to detection of general tendency of content and distribution of HMs in waters, bottom sediment of lower reaches of Kura River and bioaccumulation of toxic metals in organs and tissues of fishes of various ecological groups.

Keywords: heavy metals, bioaccumulation, microelement, monitoring, environmental pollution

INTRODUCTION

Kura River with its industrial and domestic waste is main source of drinking water in Azerbaijan. Their industrial and domestic wastes have sources outside of the borders of country that raises serious concerns. Such a situation requires high attention and development of various approaches with main goal to prevent further deterioration of its ecological status[1-4].

Heavy metals (HM) are one of the priority groups within polluting substances (PS), which affect to the ecosystem of Kura River[5,6]. It is necessary to note important HMs - pollutants, which are Cu, Zn, Mn, Cd and Cr. Domestic, agricultural and industrial waste water, including waste water of the leather, metal and mining industries are their main sources. Also, their illegal dumps appeared across the bank of Kura River as a result of absence of organized solid domestic waste (SDW) polygons is considered as additional source of the pollution.

Upon entering into the aquatic environment, HMs become part of biogeochemical cycles and start to be accumulated in the bottom sediments and various hydrobiont groups. Entering of the HMs to the aquatic organisms happens as directly from water, but also by trophic way. By migrating through trophic nets, HMs can be accumulated on their higher levels in amounts, which will be dangerous for health of both hydrobionts and human.

It is possible to assess the quality of the water basin by using the information about the microelement content of the organs and tissues of fishes. Fishes occupy the highest trophic level in the biocoenoses of aquatic ecosystems and among other hydrobionts, they have clearly exhibited ability to accumulate HMs. The increased content of metals in fish is evidence of their significant concentration in the aqueous medium, whereas, their accumulation in the food chain means functional disorders at all levels of the ecosystem. First of all, accumulation level of HMs in organs and tissues of fishes depends on hydrochemical indicators of conditions of fish habitat, then, also, it depends on their belonging to a particular ecological group (benthophage, plankton, phytophages euryphage predator) and the individual characteristics of species (age, sex, physiological state etc)[7-11].

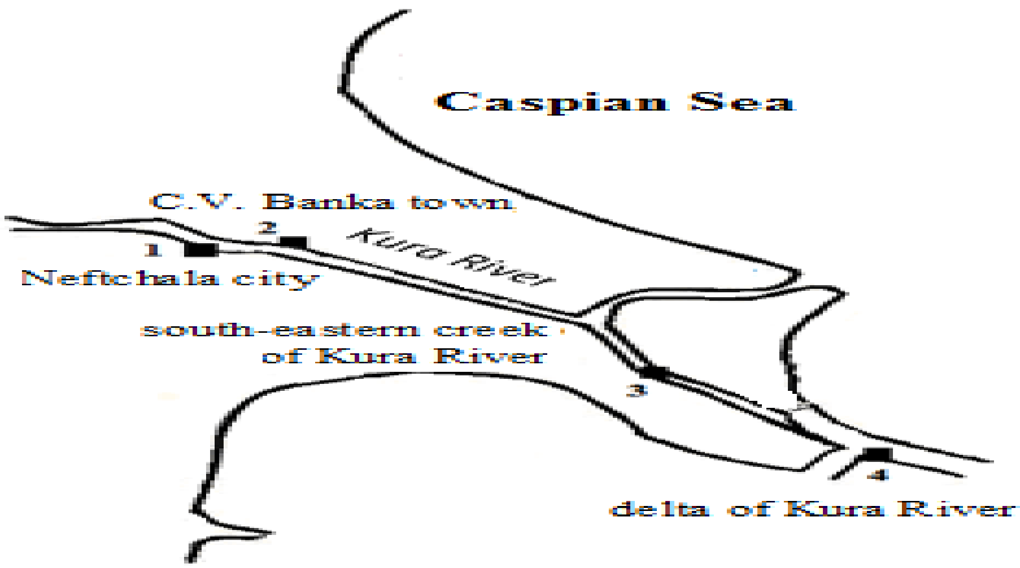
Main goal of this paper is to study general tendency on content and distribution of HMs in abiotic environment: water, bottom sediments (BS) of lower reaches of the Kura River and biotic environment, namely, bioaccumulation of the toxic metals in the organs and tissues of fishes belonging to habitants of the various ecological groups.

MATERIAL AND METHOD OF THE STUDY

Samples of water, BSs and fish, collected in four stations in lower reaches of the Kura River during spring and autumn seasons of 2011-2013 were the materials of the study (fig. 1). Samples are collected by using standard methods (with Waterbottle batometer) in the surface and nearest-bottom aquifers, but, Petersen grab with gripping area 0.025 sq.m was used for collection BS. Fish was caught by fixed gillnets (length is from 5 to 25 m, height is 0.8-1.2 m, mesh is from 28 to 70 mm) and scraper (mesh is 6x6 mm) of 20 m length.

In current paper, the results of processing of organs and tissues of 3 species of fishes (total 52 samples) belonging to various ecological groups on food are analyzed. They are the following: predator - River perch *Sander lucioperca* (Linnaeus), benthophage - monkey goby *Neogobius fluviatilis* (Pallas) and evrifag (its main food is plankton) - Kura roach *Rutilus rutilus caspicus n.kurensis* Berg.

Analysis of probes of samples of water, BS and fish tissues on existence of HMs is performed in laboratory of ecological monitoring of Baku State University. Probes are analyzed on existence of the following HMs: Cu; Zn; Ba; Al; Cd; Cr; Co; As; Fe; Mn; Mo, Ni, Zr, Sr, Ni; Pb; Hg. Water was filtered after collection of probes. BSs were dried up to dry-air state. Preparation of the probes from the samples of water and BS was performed in the microwave oven MSW-2 of company Berghof under the programmes P1 (T_1=160 ^{0}C, t_1=5 minutes, p_1=80%, T_2=200 ^{0}C, t_2=10 minutes, p_2=80%, T_3 <100 ^{0}C, t_3=10 minutes, p_3=0) and P_2 (T_1= 175 ^{0}C, t_1=10 minutes, p_1=99%, T_2=(low)100 ^{0}C, t_2=10 minutes, p_2=0%, T_3= 0 ^{0}C t_3=10 minutes, p_3=0) [10]. Fishes were dissected and then, their organs and tissues (liver, gills, muscle, gonads, brain) were dried in the drying cabinet of type 2V-151 up to constant mass at 105^{0}C.



1. Neftchala city, 2. C.V. Banka town, 3.south-eastern creek of Kura River, 4.delta of Kura River

Figure 1: Map-scheme and location of stations for collection of samples in lower reaches of the Kura River:

Dried fish tissue samples were thoroughly grounded in an agate mortar and then subjected to acid decomposition in the microwave oven MSW-2 of the company Berghof in concentrated nitric acid HNO_3 under the program P6 in 5 ml 30 % HNO_3 (T_1 -130° 8 minutes, T_2-155° 5 minutes, T_3 -170° 12 minutes, with a power equal to 80% at all stages)[12].

Obtained solutions were analyzed by the Atomic Emission Spectrometry with inductively bounded argon plasma (OES-ICP) Optima 2100 DV of the company Perkin Elmer (USA)[13].

For determination of the accumulation quantity of HMs, the coefficient of bottom accumulation (CBA) was computed, taking into account ability of polluting substances to be accumulated in BS. CBA is determined as ratio of substance concentration in BS (C_{BS}) to their concentration[14] in water (C_{water}): $CBA=C_{BS}/C_{water}$.

RESULTS OF THE STUDY

Data of the performed analysis shows an excess of maximum permissible concentration (MPC) of some metals such as Cu, Al, As, Fe, Zn and Hg of station 1 (Table 1).

Table 1: Concentration of HMs in the water of Kura River (spring monitoring 2013)

Stations	Ag	Hg	Cu	Pb	Cd	Al	Zn	Ni	Cr	Co	Mn	Sr	Fe	As	Ba
1	<0.0006	0.002	0,069	0,01	<0,0001	1,03	1,101	<0,0005	0.006	<0,0002	0.082	4,429	0,732	0,88	0.302
2	<0.0006	<0,001	0, 02	0,004	<0,0001	0.261	0.04	0,0005	0.003	<0,0002	0,07	2	0,3	0,4	0,01
3	<0.0006	<0,001	0.025	0,004	<0,0001	<0,001	0.001	0,0005	0.003	<0,0002	0,07	2	0,5	0,2	0.027
4	<0.0006	<0,001	0,001	0,004	<0,0001	<0,001	0,05	0,008	0.003	<0,0002	0,08	0,02	0,4	0,2	0,02
Max*	0,0006	0,03	0,069	0,001	0,0004	1,03	1,101	0,008	0.005	<0,0002	0,3	4,429	0,732	0,88	0.302
MPC [13]	0,05	0,0005	0.001	0,01	0,001	0,2	1	0,02	0,05	0,1	0,1	7	0,3	0,01	0,7
Detet.. limit mg/l	0,0006	0,001	0,0004	0,001	0,0001	0,001	0,0002	0,0005	0,0002	0,0002	0,0001	$0,05x10^{-3}$	0,1	0,002	$0,03\times10^{-3}$

***maximum values are observed in samples from station 1; Standard error - 10%**

Contents of HMs in BS is one of the main objective and reliable indicators of the pollution of the water basin. The system BS-nearest bottom water is very complicated and the redox processes, presence of complexing agents, pH value, temperature and etc. are its main factors of definition. Higher values of pH (8.5-9.0) and redox potential of the nearest-bottom layer of the water make diffuclties on the transition of metals from depositions to water layer.

Only the data on the concentration of substances in the water is not sufficient for complete characterization of the processes happening in the selected water objects and determination toxicological upload to the ecosystem. Here, it is necessary also to take into account the processes of accumulation of substances in BS and biological objects.

Studied samples of bottom sediments are hardened mainly by Fe and Mn, which can be observed especially in stations 2 and 4 (Figs. 2 and 3). Maximums of accumulation of all mentioned above elements are observed in station 4. Values of CBA for Cu in fact are constant for all stations of smaple collection that is consequent of the result of long-time anthropogenic influence. The rate of mobile forms of Cu as well as Zn, As and Zr is also high and this increases their toxicity.

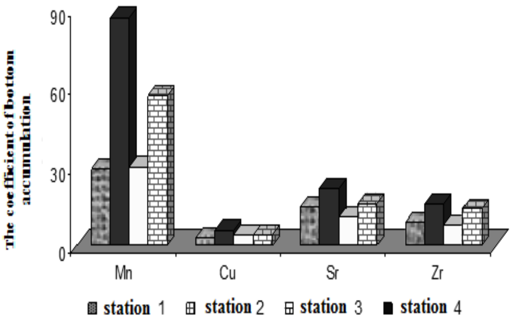


Figure 2. The coefficient of bottom accumulation of Mn, Sr, Zr and Cu in the lower reaches of Kura River (Stations 1-4)

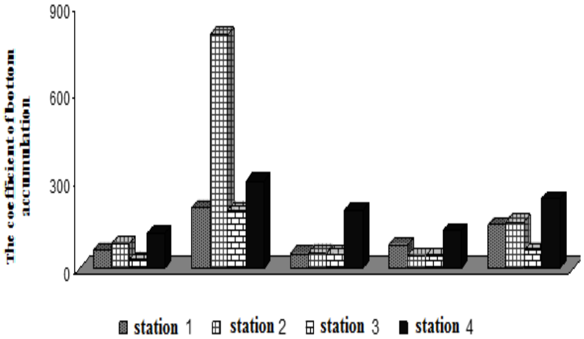


Figure 3. The coefficient of bottom accumulation of Cr, Fe, Zn, As, Ba and Al in the lower reaches of Kura River (Stations 1-4)

Interpretation of the obtained data is complicated due to existence of natural high concentration of some HMs connected with the geology of the coastal zone. Additionally, factories of the metal and mining industries as well as leather industry substantially also increase the content of metals in the water and BS. **Al** content in water was higher than MPC as well as BSs also became heavier by **Al** and it is a result of both anthropogenic influence (wastewater of the factories of metal industry) and local geochemical features.

Distribution of HMs in tissues and organs of hydrobionts is characterized by non-uniformity that is related with their functional features as well as chemical activity of the metal itself. Metals are arranged in the following row depending on their sensitivity and toxic action to the fishes: Ag > Hg > Cu > Pb > Cd > Al > Zn > Ni > Cr > Co > Mn > Sr [14].

At study of the organs and tissues of the fishes on accumulation and distribution of the metals in them, it is established specific rows on descending concentration of the metals. Ranged rows on accumulation of metals in gills and livers as well as diagrams of distribution of some metals in organs and tissues of hydrobionts are presented below:

Character of distribution of HMs by organs of **river perch (spring 2013)**:

Liver Fe> Zn > Mn >Al > Hg > Ba > Ni > Cr > Pb > Cd > Co

Gills Fe > Zn > Cu > Mn > Cr >Al > Ba >Ni > As >Pb> Cd

Table 2: Ratio of HMs in various organs and tissues of river bench during spring 2013

Organs	Fe, mg/kg	Mn, mg/kg	Zn, mg/kg	Cr, mg/kg
Brain	13,2	3,7	32	0,01
Liver	139,92	9,9	42,4	0, 45
Gills	98,3	12,7	45,6	0,5
Muscles	61,77	2,1	20,3	0,3
Gonads	69,2	8,2	3,7	0,05

Standard error is 15%

By their total content in organs and tissues of bench, microelements form the following rows (spring):

Fe liver > gills > muscles > gonads > brain

Zn gills > liver >brain > muscles > gonads

Cr gills > muscles > liver > gonads > brain

Mn gills > liver > gonads > brain > muscles

Character of distribution of HMs by organs of river perch (autumn 2013):

Liver Fe > Zn > Mo> Mn> Cu >Sr > Ni > Cr >As>Pb> Co

Gills Fe > Sr > Zn > Cu > Mo> Mn >Cr >Co>Ni > As >Pb

Table 3: Ratio of HMs in various organs and tissues of river bench during autumn, 2013

Organs	Fe, mg/kg	Mn, mg/kg	Zn, mg/kg	Cr, mg/kg
Brain	15,2	9,9	24,8	0,32
Liver	144, 2	10,1	33,8	0,65
Gills	108,3	12,1	41,6	0,78
Muscles	71,77	2,8	22,1	0,38
Gonads	7,2	1,9	3,2	0,1

Standard error is 15%

By their content in organs and tissues of bench, microelements form the following rows (Autumn 2013):

Fe liver > gills > muscles > brain > gonads

Zn gills > liver >brain > muscles > gonads

Cr gills > liver > muscles > brain > gonads

Mn gills > brain > liver > muscles > gonads

Character of distribution of HMs by organs of **Kura roach (Spring, 2013)**:

Liver Fe > Zn > Mn>Mo> Cu > Sr > Cr >Co>Ni> As >Pb

Gills Fe >Zn > Sr > Cu > Mn> Mo > Co>Ni> Cr > As >Pb

Table 4: Ratio of HMs in various organs and tissues of roach during spring, 2013

Organs	Fe, mg/kg	Mn, mg/kg	Zn, mg/kg	Cr, mg/kg
Brain	20,8	9,34	33,8	0,28
Liver	144,2	10,1	42,5	0,45
Gills	140,3	14,2	54,8	0,68
Muscles	81,78	9,8	12,1	0,52
Gonads	12,2	1,9	2,2	0,3

Standard error 15%

By their content in organs and tissues of roach, microelements form the following rows (Spring, 2013):

Mn brain > liver > gills > muscles > gonads

Zn brain > gills > liver > gonads > muscles

Fe liver > gills > muscles > brain > gonads

Cr gills > liver > muscles >gonads > brain

Character of distribution of HMs by organs of **Kura roach (Autumn, 2013)**:

Liver Fe > Zn > Mn >Mo> Sr > Cu > Cr >Co>Ni> As >Pb

Gills Fe > Zn> Sr > Mn > Cu > Mo > Cr >As >Co>Ni> Pb

Table 5: Ratio of HMs in various organs and tissues of river roach during Autumn, 2013

Organs	Fe, mg/kg	Mn, mg/kg	Zn, mg/kg	Cr, mg/kg
Brain	23,3	8,2	31,5	0,32
Liver	153,2	10,6	35,8	0,47
Gills	130,3	10,34	44,8	0,58
Muscles	22,78	3,9	12,1	0,42
Gonads	10,0	4,8	6,2	0,5

Standard error is 15%

By their total content in organs and tissues of roach, microelements form the following rows (Autumn, 2013):

Mn liver > gills > brain > muscles >gonads

Zn brain > gills > liver > gonads > muscles

Fe liver > gills > brain > muscles > gonads

Cr gills > liver > muscles > gonads > brain

Character of distribution of HMs by organs of **monkey goby (Spring, 2013)**:

Liver Fe > Zn > Mn >Mo> Cu> Sr > Cr >Co>Ni> As> Pb

Gills Fe > Zn> Sr >Mn > Mo > Cu > Cr >Co>Ni> As >Pb

Table 6: Ratio of HMs in various organs and tissues of monkey goby during Spring, 2013

Organs	Fe, mg/kg	Mn, mg/kg	Zn, mg/kg	Cr, mg/kg
Brain	20,1	10,2	14,8	0,12
Liver	94,2	15,3	34,7	0,71
Gills	89,3	10,4	40,8	0,89
Muscles	22,78	12,9	12,9	0,2
Gonads	2,2	9,8	18,1	0,9

Standard error is 15%

By their total content in organs and tissues of monkey goby, microelements form the following rows (Spring, 2013):

Mn liver > muscles> gills > gonads > brain

Zn gills > liver > gonads > brain > muscles

Fe liver > gills > muscles > brain > gonads

Cr gills > liver > muscles > gonads > brain

Character of distribution of HMs by organs of **monkey goby (Autumn, 2013)**:

Liver Fe > Zn > Mn > Mo> Sr > Cu > CoN i > Cr > As > Pb

Gills Fe > Zn > Mo>Sr Cu>Mn> Cr > Pb > Co>Ni> As

Table 7: Ratio of HMs in various organs and tissues of monkey goby during Autumn, 2013

Organs	Fe, mg/kg	Mn, mg/kg	Zn, mg/kg	Cr, mg/kg
Brain	21,3	8,2	32,3	0,23
Liver	187,3	11,6	39,8	1,47
Gills	121,4	10,34	46,8	0,91
Muscles	12,78	3,9	14,3	0,34
Gonads	9,2	4,8	16,2	0,5

Standard error is 15%

By their total content in organs and tissues of monkey goby, microelements form the following rows (Autumn, 2013):

Mn liver > gills > brain > gonads > muscles

Zn gills > liver > brain > gonads > muscles

Fe liver > gills > brain > muscles > gonads

Cr liver > gills > gonads > muscles > brain

DISCUSSION OF THE RESULTS

Unfortunately, presented ranged results level age and sex differences, however, even such generalization allows to judge on general tendencies on the localization of the elements in the tissues of fishes and highlight most dangerous ones from the HMs list for the monitoring zone under current study.

Performed research shows the complex character of the distribution of HMs in the surface waters and biot, which is explained by existence of various forms of metals in the aqueous medium. Usually, at assessment of the level of biological activity of metal ions, one need to take into account content of their mobility form.

Analysis of the obtained data detected the following results:

Concentration of **Mn** in gills and all internal organs is explained as influence of geochemical characteristics of the territory and anthropogenic influences (wastewater from mining and metal industry factories).

Maximal concentration of **Cr** is also observed in gills as a result of anthropogenic action (leather industry etc.) due to that actually, gills are organs being in interaction with external environment.

Cu and **Zn** are characterized both with high chemical activity and high accumulation efficiency in the seaweed and plankton that defines their special importance for biot [15-17]. In our study, increased concentration of Cu and Zn are detected in both liver and gills that is related with high value of them in water.

Spring monitoring in station 1 showed existence of **Hg** in all tissues of perch (~0.3 mg/kg) that is one of the most toxic metals in ecosystem. This is evidence of existence of **Hg** in its mostly toxic form – methylmercury, whereas, unlimited Hg is accumulated mainly in liver and kidneys. Autumn monitoring did not find any evidence of existence of Hg in organs and tissues of fishes.

Nickel and **Cobalt** are not widely distributed polluting elements in BS of water systems. Unlike other HMs, tendency of Nickel and Cobalt to complex formation is less highlighted. Comparatively small mobility of these elements leads to sufficiently uniform distribution in natural objects.

Increased content of **Arsenic** (a slight excess of MPC) observed in a water and all tissues of perch (0.3-1.2 mg/kg) during the Spring monitoring (station 1) can be explained by the flood covering agricultural soils already polluted by pesticides and wastewater from various industrial factories located near of them. During autumn monitoring, decrease of concentration of Arsenic in a water was observed, which is explained by the water consumption of plankton during its intensive summer body development.

Unlike autumn monitoring, during spring one, low content of Lead was observed in the water. However, due to its high toxicity, observation of the concentrations of Pb higher than MPC of Pb concentration in organs of hydrobionts raises serious concerns.

As a result of monitoring in Station 1, it was observed that content of Al in water, BS and hydrobionts (bench) is comparable with MPC values ~30 mg/kg. Al ions are toxic for most of the water organism species. But, high concentration of Al in bottom sediments perhaps is a result of geochemical feature of the area – existence of clayey soil.

We provided comparative analysis of distribution and accumulation of HMs in various forms of ecosystem of water basin of Kura River based on average spring and autumn monitoring of water samples, BS as well as tissues and organs of hydrobionts.

CONCLUSIONS

BSs and hydrobionts are reliable indicators of state of ecosystem thanks to their behavior as concentrators of persistent toxicants. Pollution of water basins by compounds of HMs is widely distributed form of the anthropogenic action. Many HMs are biologically active and are accumulated in sufficiently high concentrations in tissues of hydrobionts. Spring flood explains increase on concentration of some toxicants in water during spring.

Analysis of obtained by us data shows that Fe and Mn mostly are concentrated in gills as well as Fe also is concentrated in livers and Cu is concentrated in muscles and livers and partly in gonads. It is believed that very toxic metals Pb, Cd, Hg mainly are concentrated in gills and heart [17]. Obtained by us data showed maximal concentration of Pb in gills and gonads. Content of Pb in gonads of monkey goby excesses MPC and changes in range 0.4-1.5 mg/kg. This fact raises serious concern, because, it can lead to mutations in next generations.

Usually, heavy metals are concentrated in organisms together and at determination of their level of toxicity in the ecosystem, it is necessary to take into account not only MPC of individual metal, but, also features of their interaction and joint action to biological systems.

Thanks to high level of mineralization of waters of Kura River, toxicity of most of metals is less than allowed threshold, /high concentration of ions of such metals as Ca and Mg prevents accumulation of toxic HMs by hydrobionts and subsequently decreases their toxic influence.

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