



HEAVY METAL POLLUTION OF THE CATCHMENT BASINS OF THE VOGHCHI AND MEGHRIGET RIVERS (ARMENIA) AND RISKS TO THE ENVIRONMENT ASSOCIATED WITH WATER POLLUTION

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Heavy metal and aluminum pollution of the hydroecosystems in the catchment areas of the Voghchi and Meghriget rivers and risks to the environment associated with water pollution were investigated. The catchment areas of the Voghchi and Meghriget rivers are situated in the south of the Republic of Armenia where mining and metallurgical industries are highly developed. The investigations revealed that the Voghchi, Geghi, Artsvanik and Meghriget rivers were polluted with heavy metals and aluminum. Comparatively high concentrations of heavy metals and aluminum in the studied rivers were registered after Qajaran, Kapan and Meghri towns and the tailings storage facility of Artsvanik which may have been conditioned by the influence of wastewaters from urban mining and metallurgical and domestic activities. The assessment of changes in the species composition of phytoplankton community performed by the Menhinick diversity index revealed that ecosystem conditions were deteriorated in the Voghchi river after Kapan town and the Artsvanik river after the tailings storage facility which may have been conditioned by heavy metal and aluminum pollution.

Keywords: Rivers, Heavy metal and aluminum pollution, Mining and metallurgical and domestic activities, Phytoplankton community, Menhinick diversity index.

Introduction

The pollution of the aquatic environment with heavy metals has become a worldwide problem during recent years, because they are indestructible and most of them have toxic effects on organisms.

Among environmental pollutants, metals are of particular concern, due to their potential toxic effect even at low concentrations and ability to bioaccumulate in aquatic ecosystems [5].

Contamination of a river with heavy metals may have devastating effects on the ecological balance of the aquatic environment, and the diversity of aquatic organisms becomes limited with the extent of contamination [6].

The hydroecosystems in the catchment areas of the Voghchi and Meghriget rivers are endangered by heavy metal pollution.

The catchment areas of the Voghchi and Meghriget rivers are situated in the south of the Republic of Armenia where mining and metallurgical industries are highly developed. In these areas, the waste and wastewater management insufficient situation is a serious environmental problem. For a long

time, the sewer systems have been in very bad conditions, the tailings storage facilities have been filled up with mining and metallurgical industrial wastewaters, the biological water cleaning stations haven't been working as a result of which wastewaters without a sufficient cleaning have been flowing into the aquatic ecosystems of the areas [3].

The present study was aimed at investigating heavy metal and aluminum pollution of the hydroecosystems in the catchment areas of the Voghchi and Meghriget rivers and risks to the environment associated with water pollution.

Materials and Methods

The objects of this study were the Meghriget, Voghchi and its main tributaries - Geghi and Artsvanik rivers. Water samples were collected once a season during 2008-2009. The samples were taken from the 8 sites of the Voghchi, Geghi, Artsvanik and Meghriget rivers (Figure. 1).

The sites were selected in such parts of the rivers where qualitative changes in water were expected.

The analyses of heavy metals and aluminum concentrations and phytoplankton parameters were done by the standard methods accepted in hydrochemical and hydrobiological studies.

The concentrations of heavy metals and aluminum in the water samples were determined by the mass spectrometric method using ELAN 9000 inductively coupled plasma mass spectrometer (ICP-MS) [2].

For the phytoplankton study, the 1 litre water sample taken from each site was fixed with 40% formaldehyde solution (0.4% final concentration) immediately and stored in a dark place. The further study was carried out under laboratory conditions [1, 7].

The qualitative and quantitative analyses of phytoplankton were executed by a microscope in the Nageotte chamber ($V = 0.1\text{ml}$).

The assessment of changes in the species composition of phytoplankton community was performed by the Menhinick diversity index. [1, 4]



Sampling sites

1. Voghchi – 1.7 km before Qajaran town,
2. Voghchi – 1.7 km after Qajaran town,
3. Voghchi – 0.8 km before Kapan town,
4. Voghchi – 6.8 km after Kapan town,
- 1'. Geghi – river mouth,
- 1''. Artsvanik – river mouth (after the Artsvanik tailings storage facility).
1. Meghriget - 0.5 km before Meghri town,
2. Meghriget – river mouth (after Meghri town).

Figure 1. Schematic map of the selected sampling sites in the catchment areas of the Voghchi and Meghriget rivers.

Results and Discussion

As shown in Figures 2 - 19, comparatively high concentrations of heavy metals and aluminum in the Meghriget and Voghchi rivers were observed after Meghri and Qajaran, Kapan towns respectively which is explained by the influence of wastewaters from the mining and metallurgical industries of Qajaran and Kapan towns as well as domestic sewage from Qajaran, Kapan and Meghri towns. A drastic increase in the concentrations of heavy metals and aluminum in the Voghchi river waters was observed after Kapan town where the river were subjected not only to the influence of urban mining and metallurgical industrial and domestic wastewaters but also to the pressure of its tributary – the Artsvanik river.

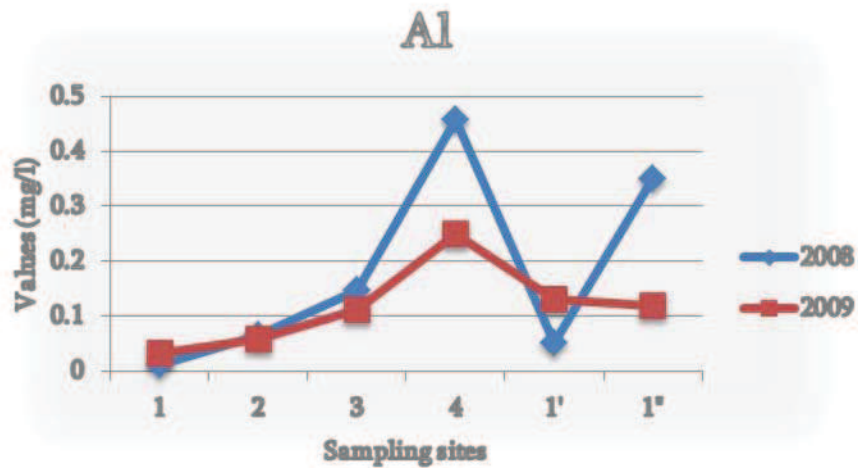


Figure 2. Dynamics of the mean annual concentration of aluminum in the Voghchi, Geghi and Artsvanik rivers according to the flow.

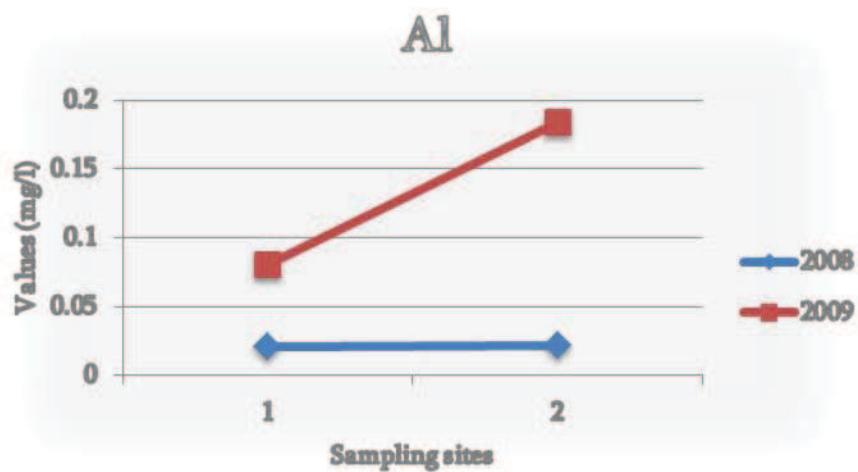


Figure 3. Dynamics of the mean annual concentration of aluminum in the Meghriget river according to the flow.

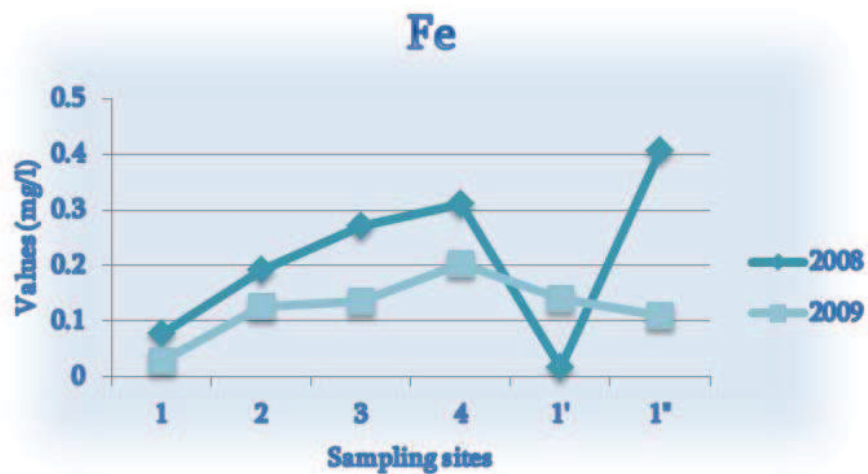


Figure 4. Dynamics of the mean annual concentration of iron in the Voghchi, Geghi and Artsvanik rivers according to the flow.

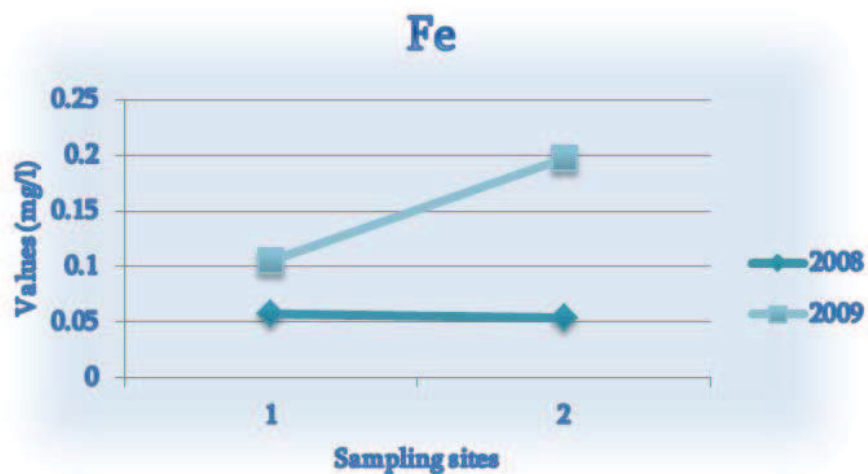


Figure 5. Dynamics of the mean annual concentration of iron in the Meghriget river according to the flow.

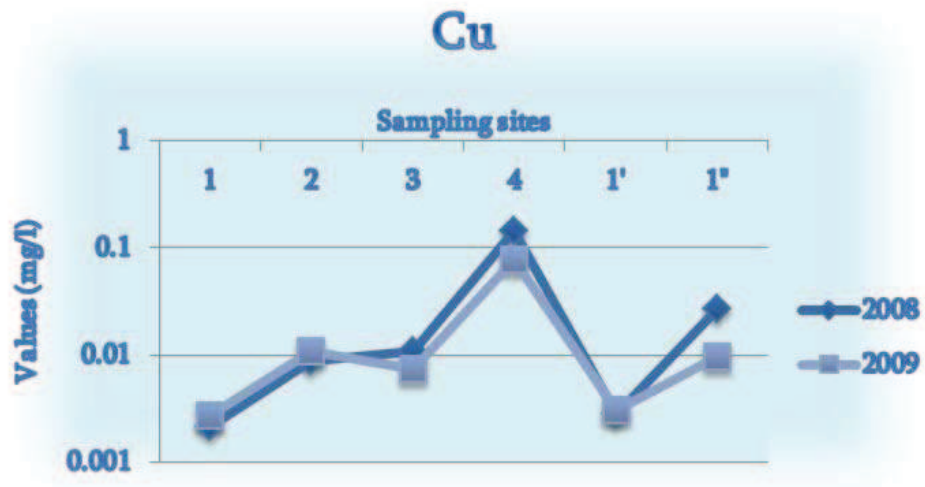


Figure 6. Dynamics of the mean annual concentration of copper in the Voghchi, Geghi and Artsvanik rivers according to the flow.

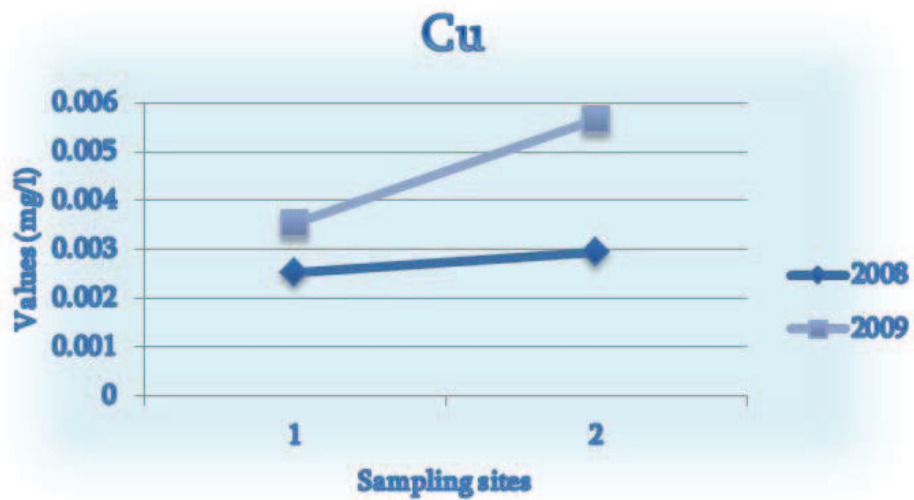


Figure 7. Dynamics of the mean annual concentration of copper in the Meghriget river according to the flow.

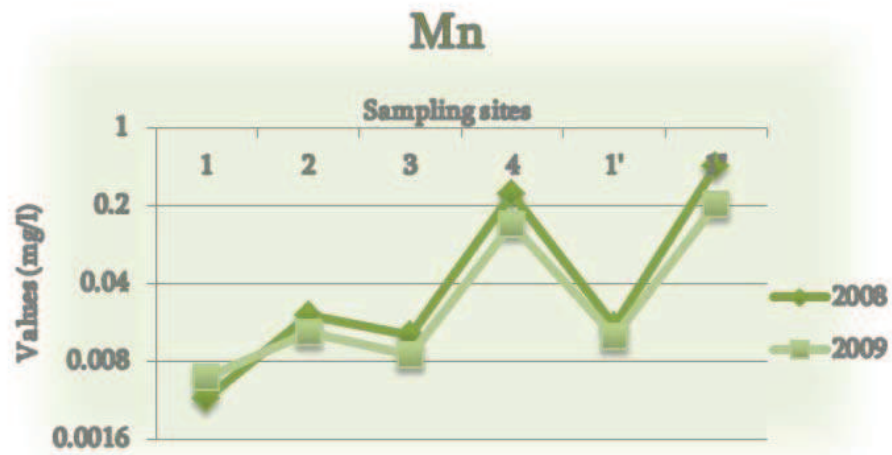


Figure 8. Dynamics of the mean annual concentration of manganese in the Voghchi, Geghi and Artsvanik rivers according to the flow.

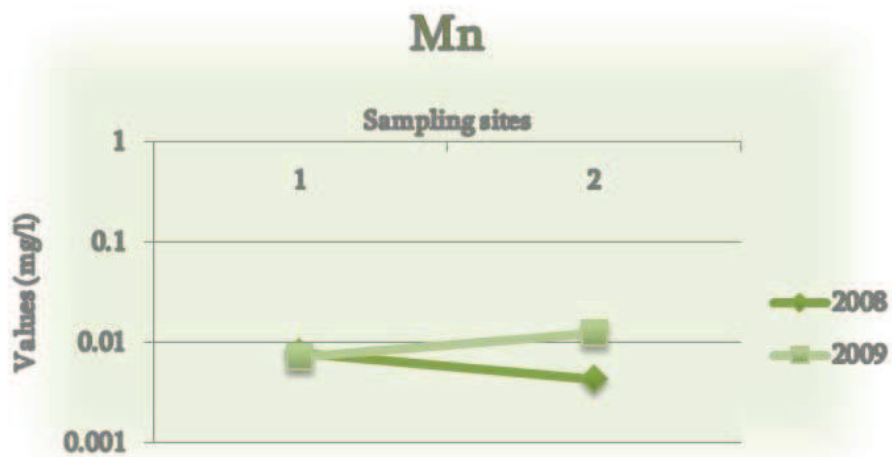


Figure 9. Dynamics of the mean annual concentration of manganese in the Meghriget river according to the flow.

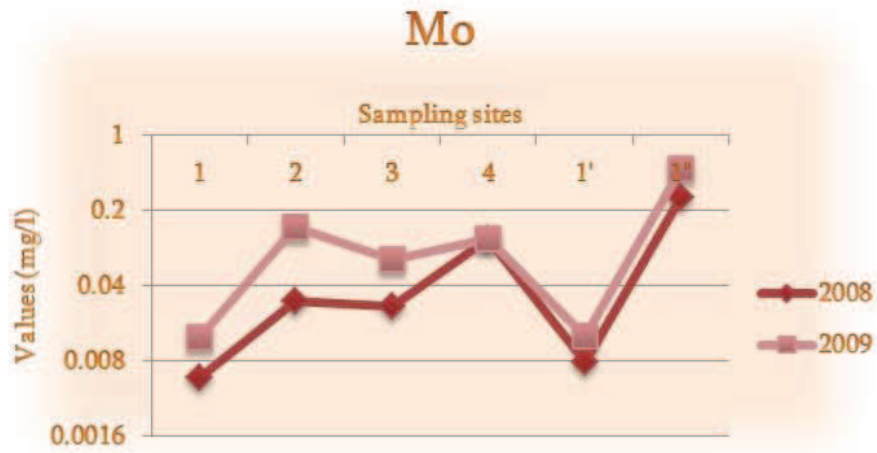


Figure 10. Dynamics of the mean annual concentration of molybdenum in the Voghchi, Geghi and Artsvanik rivers according to the flow.

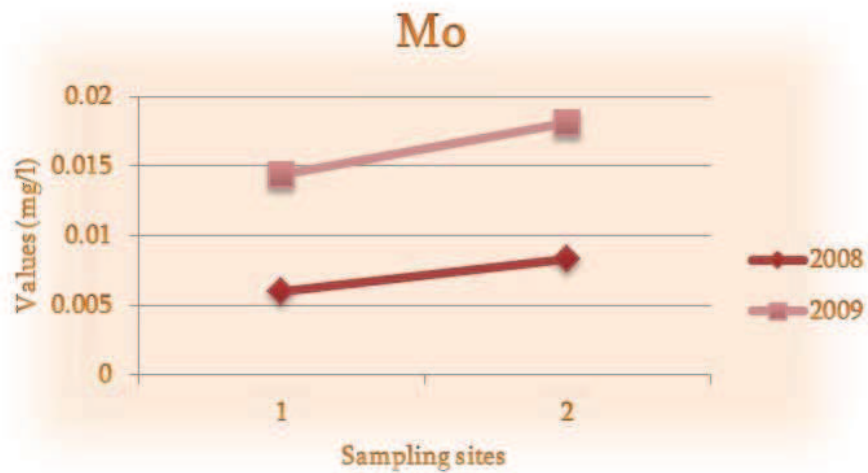


Figure 11. Dynamics of the mean annual concentration of molybdenum in the Meghriget river according to the flow.

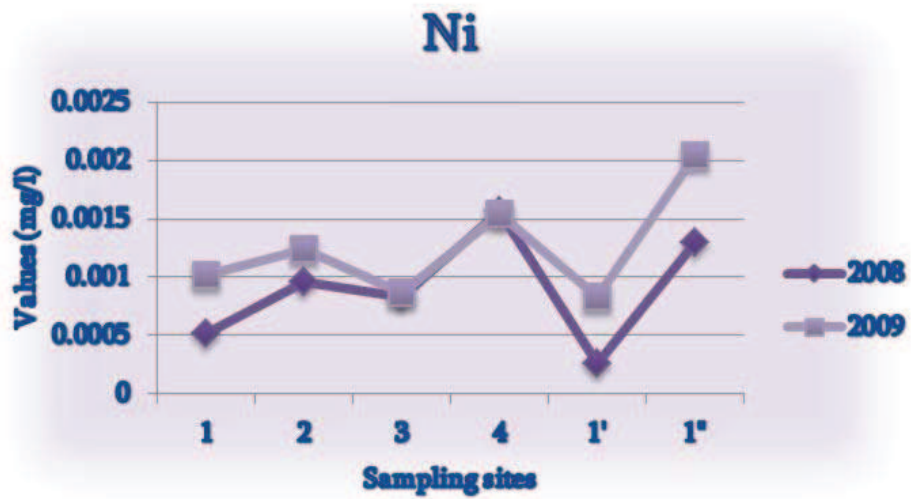


Figure 12. Dynamics of the mean annual concentration of nickel in the Voghchi, Geghi and Artsvanik rivers according to the flow.

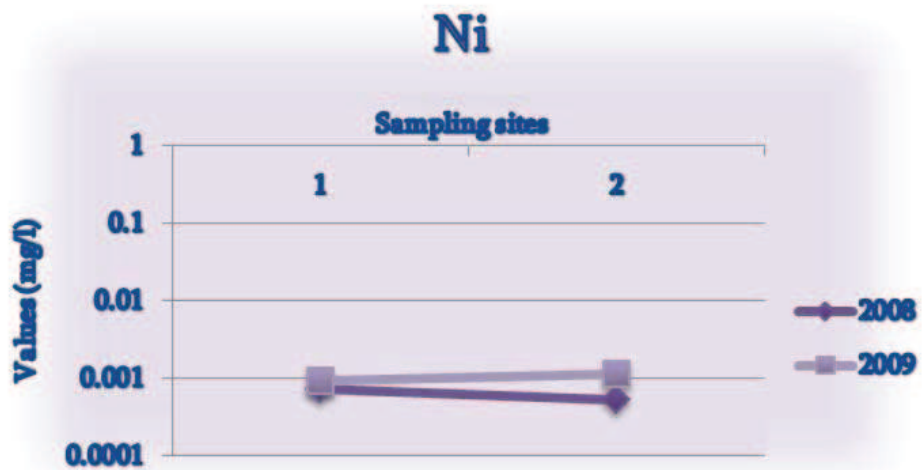


Figure 13. Dynamics of the mean annual concentration of nickel in the Meghriget river according to the flow.

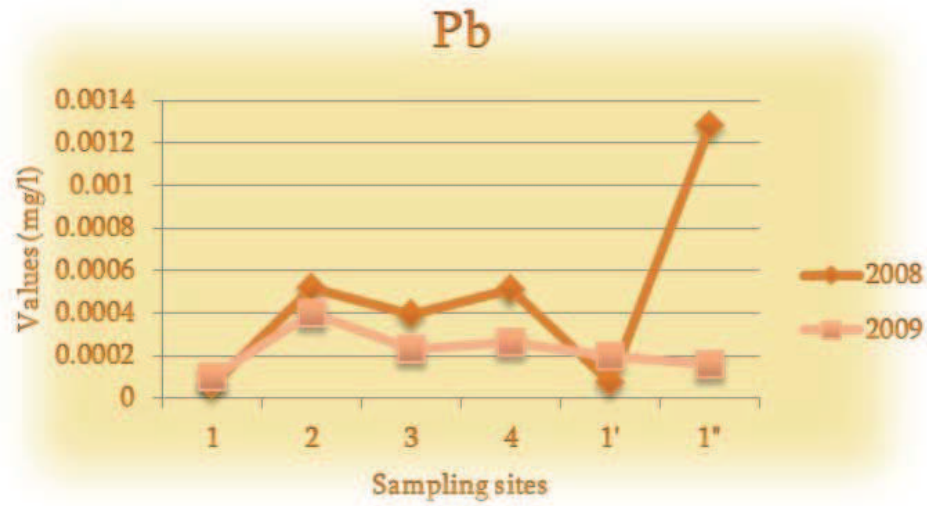


Figure 14. Dynamics of the mean annual concentration of lead in the Voghchi, Geghi and Artsvanik rivers according to the flow.

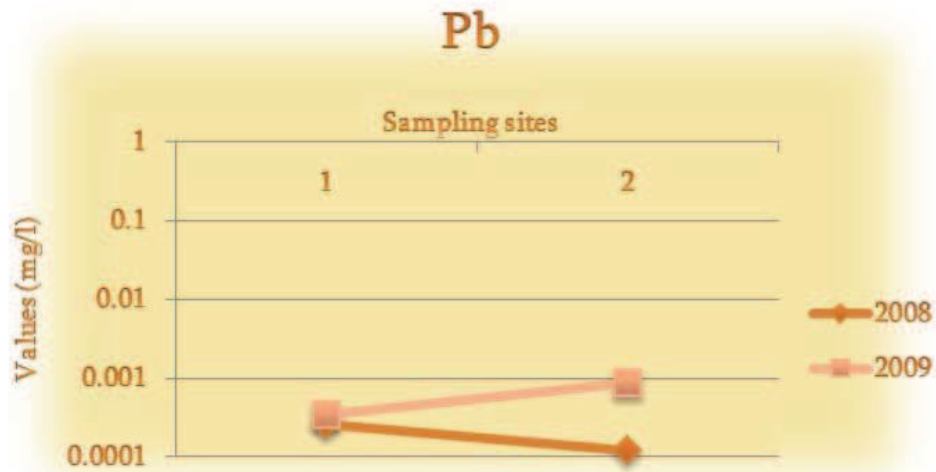


Figure 15. Dynamics of the mean annual concentration of lead in the Meghriget river according to the flow.

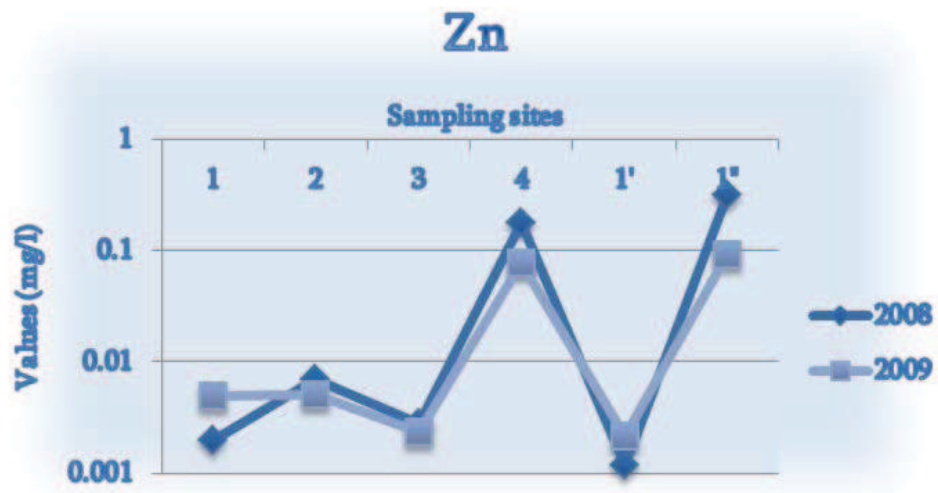


Figure 16. Dynamics of the mean annual concentration of zinc in the Voghchi, Geghi and Artsvanik rivers according to the flow.

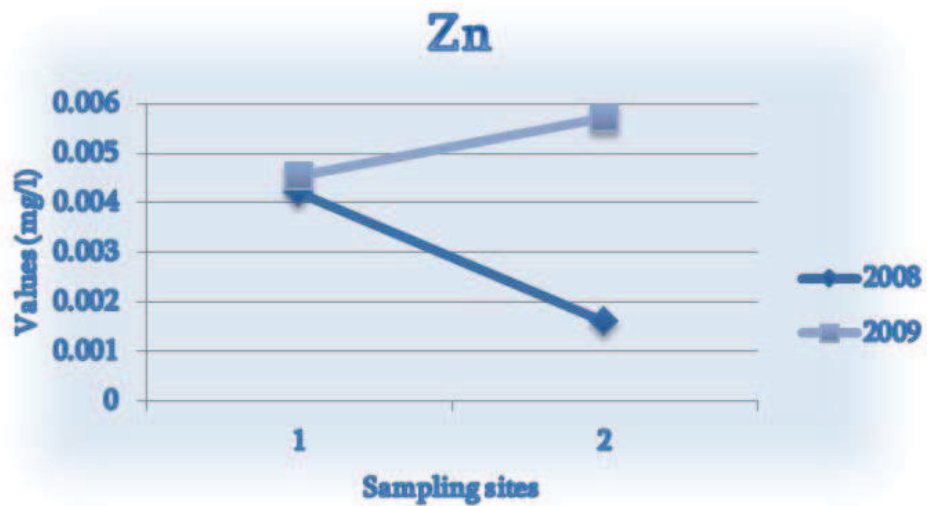


Figure 17. Dynamics of the mean annual concentration of zinc in the Meghri river according to the flow.

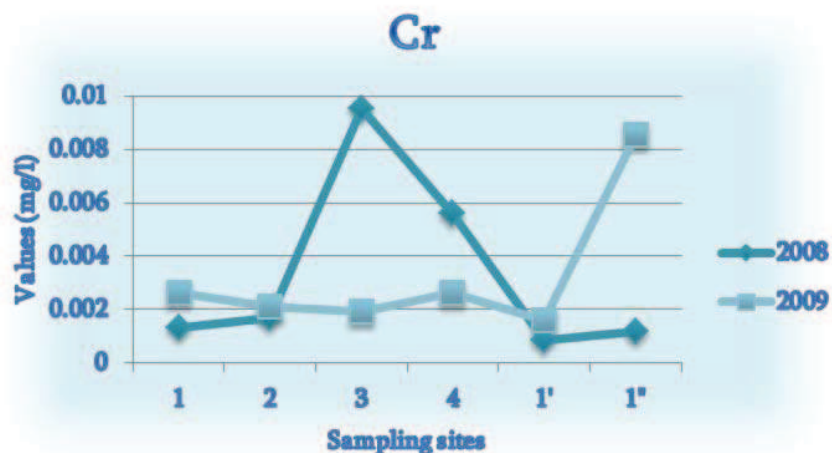


Figure 18. Dynamics of the mean annual concentration of chromium in the Voghchi, Geghi and Artsvanik rivers according to the flow.

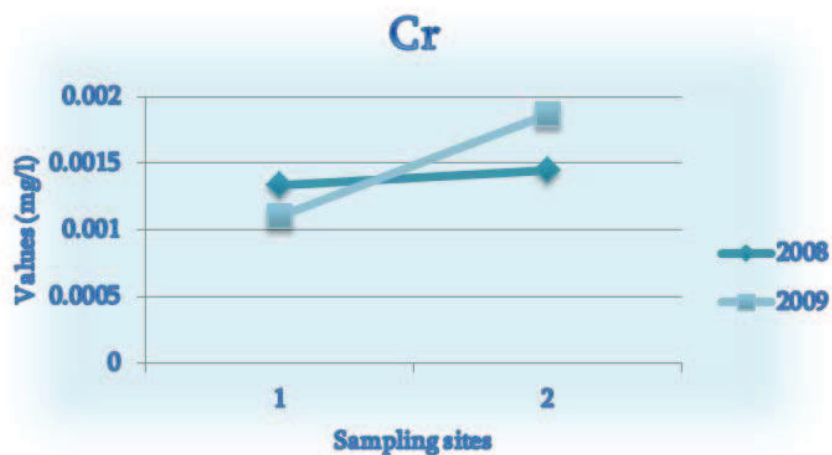


Figure 19. Dynamics of the mean annual concentration of chromium in the Meghriget river according to the flow.

The highest level of heavy metal pollution was registered in the Artsvanik river mouth after the tailings storage facility of Artsvanik where wastewaters from the mining and metallurgical industries of Qajaran and Kapan towns were collected and stored causing the pollution of the Artsvanik river waters which also affected the quality of the Voghchi river waters, especially after Kapan town. The lowest pollution level was observed in the mouth of the Geghi river which flowed through an area that wasn't under high anthropogenic pressure (Figures. 2 - 19).

Table 1. Heavy metals and aluminum concentrations (mg/l) in the Voghchi river waters during 2008 -2009.

Heavy metals	Sampling sites				Standards, mg/l (Armenia)
	1	2	3	4	
Al	0.004126 - 0.073710	0.013961 - 0.143510	0.017758 - 0.313200	0.099910 - 0.716710	0.040
Fe	0.000286 - 0.099166	0.029554 - 0.285043	0.036046 - 0.550644	0.041029 - 0.515380	0.500
Cu	0.001409 - 0.003851	0.003518 - 0.015254	0.004715 - 0.018623	0.039665 - 0.298650	0.001
Mn	0.001288 - 0.009144	0.001533 - 0.039460	0.002257 - 0.024338	0.066439 - 0.402719	0.010

<i>Mo</i>	0.001883 - 0.041115	0.022428 - 0.268182	0.017598 - 0.162563	0.019179 - 0.230066	0.500
<i>Ni</i>	0.000080 - 0.001254	0.000564 - 0.001974	0.000288 - 0.001465	0.001094 - 0.002373	0.010
<i>Pb</i>	0.000016 - 0.000140	0.000110 - 0.000851	0.000032 - 0.001198	0.000076 - 0.001361	0.010
<i>Zn</i>	0.000418 - 0.006883	0.000486 - 0.019834	0.000295 - 0.004304	0.042088 - 0.356327	0.010
<i>Cr</i>	0.000120 - 0.008860	0.000231 - 0.006652	0.000333 - 0.032630	0.000267 - 0.018073	0.001

Table 2. Heavy metals and aluminum concentrations (mg/l) in the waters of the Geghi and Artsvanik rivers during 2008 – 2009.

<i>Heavy metals</i>	<i>Sampling sites</i>	
	1'	1''
<i>Al</i>	0.010508 - 0.409483	0.065057 - 0.557341
<i>Fe</i>	0.002694 - 0.487703	0.047812 - 1.338889
<i>Cu</i>	0.001229 - 0.005608	0.005852 - 0.037220
<i>Mn</i>	0.003179 - 0.039053	0.054078 - 0.944170
<i>Mo</i>	0.002096 - 0.032848	0.074556 - 1.164416
<i>Ni</i>	0.000083 - 0.001164	0.000789 - 0.003146
<i>Pb</i>	0.000007 - 0.000516	0.000007 - 0.003140
<i>Zn</i>	0.000046 - 0.003175	0.040895 - 0.408699
<i>Cr</i>	0.000013 - 0.004498	0.000056 - 0.032754

Table 3. Heavy metals and aluminum concentrations (mg/l) in the Meghriget river waters during 2008 – 2009.

<i>Heavy metals</i>	<i>Sampling sites</i>	
	1	2
<i>Al</i>	0.004346 - 0.266692	0.002688 - 0.351240
<i>Fe</i>	0.021258 - 0.325218	0.016023 - 0.362426
<i>Cu</i>	0.001111 - 0.008096	0.001669 - 0.011250
<i>Mn</i>	0.002749 - 0.018062	0.001256 - 0.024883
<i>Mo</i>	0.003710 - 0.039599	0.005258 - 0.047302
<i>Ni</i>	0.000256 - 0.001809	0.000233 - 0.002034
<i>Pb</i>	0.000017 - 0.000996	0.000023 - 0.001462
<i>Zn</i>	0.001267 - 0.007978	0.000102 - 0.012301
<i>Cr</i>	0.000048 - 0.004444	0.000012 - 0.006015

Maximum permissible concentration of iron, copper, manganese, molybdenum, zinc, chromium and aluminum was exceeded in the studied rivers. It is necessary to mention that copper exceeded the maximum permissible concentration up to 299 times. This can be considered as extreme pollution (Tables 1, 2 and 3).

Abovementioned discussions allow us to suppose that the studied rivers were polluted with heavy metals and aluminum which may have had its negative impact on the morpho-functional parameters of hydrobionts causing significant changes in the species composition of hydrobiont communities.

Simultaneous increase in the primary production and the species diversity of phytoplankton community is considered as an index of ecological progress in case of which the Menhinick diversity index has a small value. This was not observed in the Voghchi river after Kapan town and the Artsvanik river after the tailings storage facility which indicated that the ecosystem conditions in the abovementioned sampling sites of the rivers were deteriorated (Figures. 20 and 21). Metabolic progress of phytoplankton cenosis was registered on account of the ecological regression of community.

Such ecological conditions of hydroecosystems are possible threat to human health as heavy metals have tendency to accumulate in the various organs of aquatic organisms, which in turn may enter into human metabolism through consumption causing serious health hazards.

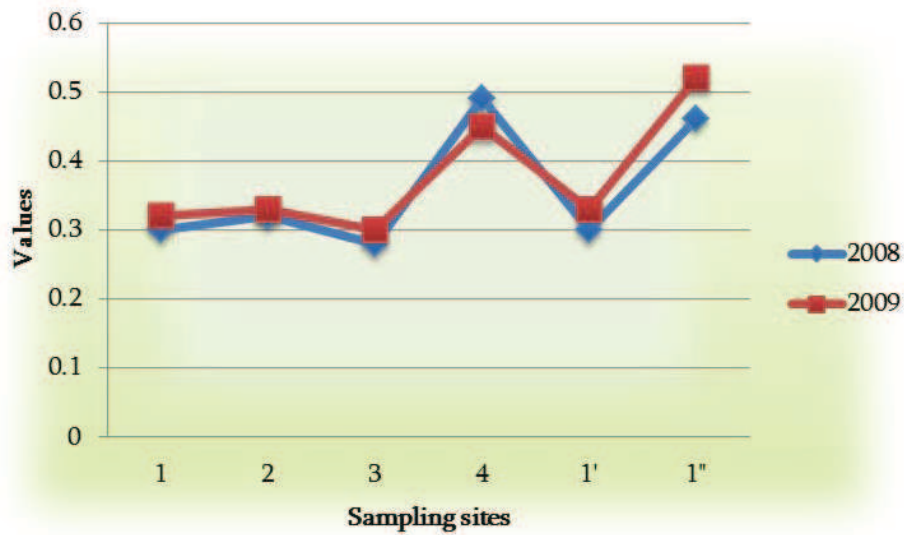


Figure 20. Dynamics of the mean annual values of the Menhinick diversity index in the Voghchi, Geghi and Artsvanik rivers according to the flow.

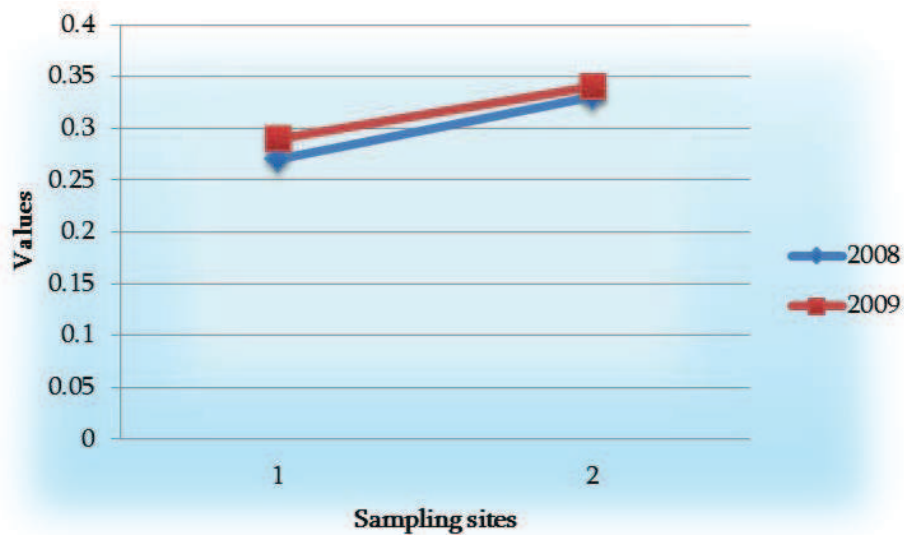


Figure 21. Dynamics of the mean annual values of the Menhinick diversity index in the Meghriget river according to the flow.

Conclusions

The investigations revealed that the Voghchi, Geghi, Artsvanik and Meghriget rivers were polluted with heavy metals and aluminum. Comparatively high pollution level of heavy metals and aluminum in the studied rivers were registered after Qajaran, Kapan and Meghri towns and the tailings storage facility of Artsvanik which may have been conditioned by the influence of wastewaters from urban mining and metallurgical and domestic activities. The lowest pollution level was observed in the Geghi river which wasn't under high anthropogenic pressure.

The assessment of changes in the species composition of phytoplankton community performed by the Menhinick diversity index revealed that ecosystem conditions were deteriorated in the Voghchi river after Kapan town and the Artsvanik river after the tailings storage facility which may have been conditioned by heavy metal and aluminum pollution.

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