



Original researches

The Patterns of Heavy Metals Accumulation in Water, Soil and their Transfer in the Soil–Plant System in the Catchment Area of the Sotk and Masrik Rivers

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Abstract. The problem of pollution of the catchment area of the Masrik river, located in the basin of lake Sevan, is associated with the gold mining plant in the basin of its Sotk tributary, where ore is mined and crushed. Industrial activity changes the natural background of the formation of the quality of various media within the river basin in terms of the heavy metals content in them. Geo-ecological studies in areas of mining activity are relevant from the point of view of assessing the level of pollution and environmental quality control. The object is the drainage basin of the Masrik river with the Sotk tributary that flows near the territory of the gold ore plant. The subject of research is heavy metals in various environments – in water, soil, plants, their behaviour, accumulation and transfer. The contents of Cu, Zn, Pb, Cr, Co, Cd and Ni were determined in water samples, floodplain soils and plants collected in the basins of the Sotk and Masrik rivers. The regularity of the prevalence of summer concentrations of copper over spring was established. It is associated with the difference in water flow in the river, when summer low water is characterized by a sharp decrease in the water content of the rivers. Lead is characterized by the predominance of spring concentrations in the upper reaches of the Sotk river and summer concentrations in the lower reaches of the Masrik River basin. This trend can be due to the washout of storm drains in spring in the Sotk River basin, which is characterized by steep banks and accumulation in the summer period in the flat part of the Masrik river. In general, for both seasons, zinc and nickel differ in relatively high concentrations. According to studies, the values of the distribution coefficient of heavy metals in soils showed a dependence on pH level. The distribution coefficients increased with decreasing acidity values. Pb was among the highest coefficients studied, and the minimum values were typical for Cu. The obtained values of the distribution coefficient indicate that copper has a high solubility and, under favourable conditions, passes into the soil solution. High lead coefficients indicate its low solubility and high adsorption in the soil. The results of the trends analysis and revealed patterns confirmed the presence of a high level of copper solubility in the soil, as well as the significant bioavailability of this metal to plants. For lead, trends of low solubility in soil have been found, but on the issue of bioavailability to plants, it exhibits ambiguous behaviour. Nickel, in terms of accumulation of soil–plant migration in the soil, shows the lowest chemical activity.

Keywords: heavy metals; pollution; accumulation; transfer.

Introduction

Economic activity in the river basins has a negative impact on the water and soil quality in catchments. The consequences of such impacts can be most pronounced in the small rivers ecosystems, which are more vulnerable due to small volumes of runoff, seasonal fluctuations in water flow. The patterns of accumulation and transfer of heavy metals under mining pollution conditions are interesting.

The problem of the catchment area pollution of the Masrik river, located in the basin of Lake Sevan, is associated with the gold mining enterprise in the tributary Sotk basin, where ore is mined and crushed. Industrial activity changes the natural background of the formation of the environment components quality within the river basin in terms of the heavy metals content in them. That is why environmental studies in the “water–soil–plant” system are relevant in this drainage basin under constant technogenic impact.

The famous scientist P. M. Kaplanian led a long – term assessment of the quality of soils, waters and bedrocks in Armenia. The

scientist conducted a study of the microcomponent composition of various environment components in the Lake Sevan basin in the system “rocks – groundwater – surface water – soil – lake water – bottom sediments”. The material obtained was summarized in the monograph “Geochemistry of natural waters of the Lake Sevan basin” published in 1997 (Kaplanyan et al., 1997). The patterns of biological absorption of elements in various geochemical types of landscapes were considered and discussed in the works of G. V. Shaginyan and R. A. Burnutyan (1988).

Testing the water quality of the Masrik river and its tributary Sotk, conducted in 2012–2014, did not show significant contamination of the waters with heavy metals (Hambaryan, 2015). Concentrations of the studied heavy metals were within acceptable environmental standards and corresponded to acceptable (1 and 2) quality classes, according to the adopted system approach of the basin management of river catchments in Armenia.

The aim of the research is to identify patterns of heavy metals transfer and the level of their accumulation in environment components.

Material and methods

The object of our research was the drainage basin of the Masrik river with its tributary Sotk. The Masrik river originates from the peaks of the Sevan range at an altitude of 2880 m. The length of the river is 45 km, the catchment area is 685 km². The river has 20 tributaries with a length of at least 10 km. In the upper course, the floodplain is narrow, V – shaped, on average it expands, and in the lower course it merges with the Masrik plain. Due to the artificial drainage of lake Gilly, which

was located in the river basin, the Masrik river currently flows into lake Sevan along an artificially dug bed. River flow is regulated. Water is used for irrigation. The river nourishment is mainly underground (78%). The highest water level is observed in spring – 36% of the annual flow (Krylov, 2010).

The bed of the Masrik river in the mountainous conditions of the basin is of irregular nature. The flood plain is developed only within the limits of the flat current. There is a change in the types of channels on the longitudinal profile of the watercourses – from mountainous to flat-meandering, with pronounced shallows and stretches. The river has great erosive power. Differences in temperature and precipitation by seasons and heights are the cause of uneven runoff. The spring flood is one of the main phases of the water regime of the river. There is a sharp decrease in runoff in the summer.

The Sotk river (the main tributary of the Masrik river) originates at the pass of the same name from absolute elevations of about 2500 m. The catchment area of the river is 18.5 km². It is strongly dissected by deep V-shaped erosion and tectonic valleys. The slopes are characterized by a large steepness and are covered with grass vegetation (Mkrтчjan, 1962, 1974). From geological points of view Meso-Cenozoic intrusive rocks and alluvial deposits covering them are widely spread: eluvial-diluvial, man-made and alluvial-proluvial sediments. They are represented by sandy-loamy, detrital and sandy-gravel varieties of soils. The source of groundwater supply is precipitation. The precipitation annual amount in the described area is 500 mm, and evaporation – 250 mm (Bagdasarjan, 1990). The waters of the Sotk and Masrik rivers were investigated at nine points (figure), the soils at three sampling points and the samples of indicator plants at two points – 2 and 8. Sampling, conservation, storage

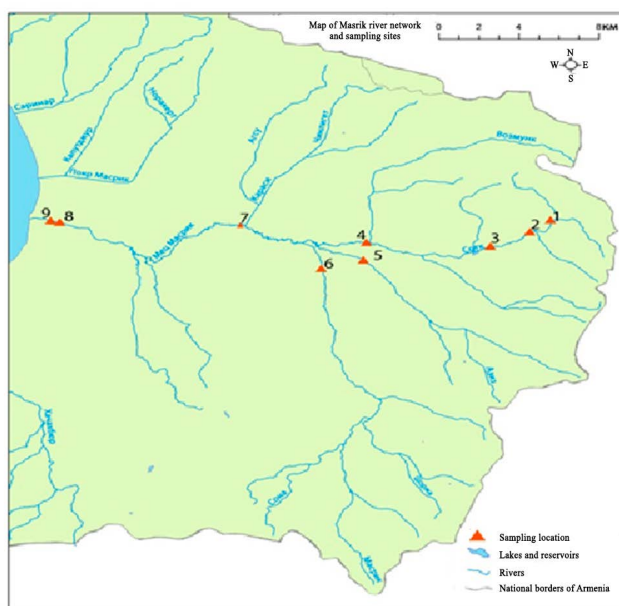
and field work were carried out according to standard operating procedures work, storage and delivery of samples to the laboratory (ISO-5667-1, ISO-5667-2, ISO-5667-3).

The temperature of the river water, the reaction of the medium (pH) and the electrical conductivity were measured on site. The remaining analyzes were performed in the laboratory in samples delivered to the laboratory in accordance with the requirements of the standards. In river water, heavy metals were determined using classical methods of analysis. Ni and Cr were determined by a colorimetric method according to ISO 8288 and ISO 11083, Cu, Pb, Zn and Cd – using a heavy metal-analyzer (Polarograph).

The method of atomic absorption spectrophotometry (AAS) is one of the most convenient and express methods for the determination of trace elements in the soil. The determination of trace elements (in our case, heavy metals) of copper, zinc, cadmium, lead, nickel, cobalt, chromium was carried out using the AAS method (Prajs, 1976) on an AAS-1N spectrophotometer of the company Carl Zeiss, Germany. Techniques allow setting the content of the above metals in the range from 0.0005% to 20%. The sample to be analyzed is fed propane-butane to the burner flame and the atomic absorption of the resonant radiation was measured by the neutral atoms of the elements being detected, which are formed during the atomization of the sample. The source of resonant radiation was a full-cathode spectral lamp. The atomic absorption of elements is determined by the most sensitive resonant spectral lines: for copper – 324.75 nm; zinc – 213.86 nm; cobalt – 240.73 nm; Nickel – 232 nm; lead – 283.3 nm; cadmium – 228.0 nm; iron – 248.3 nm; manganese – 279.48 nm; chromium – 357.87 nm (Poluektov, 1967; Havezov & Calev, 1983; Pupyshev, 2009).

The dissolution of the soil sample was carried out in a ratio of 1:5 to determine the heavy metals in the soil extract and uniformly divided the amount of the resulting solution according to the number of components to be determined.

Comparison of different sample preparation methods showed that dry ashing gives better reproducibility. The method of dry ashing was to ash 2 g of the sample at 500 °C for 4 hours. The ash residue was twice treated after cooling with 5 ml of 6 M HCl by slow evaporation to dryness in a water bath. The residue was dissolved by heating in 0.1 M HCl, filtered through a large-pore filter into a 50 ml volumetric flask. The precipitate was washed and diluted to the mark with 0.1 M HCl. The Cu, Zn, Pb, Cd, Mn, Co, Ni meaning



Sampling points:

1. Sotk River – at the gold factory;
2. Sotk River – 1.5 km downstream after the factory;
3. Sotk River – after the factory, the first bridge;
4. Sotk River – agricultural territory;
5. The left tributary of the Masrik River-Aziz, under the bridge;
6. Masrik River – near the village of Shatvan;
7. Masrik River not far from village Metz Masrik;
8. Masrik River – before the Gilly Bridge;
9. Masrik River – after the Gilly Bridge.

Picture. Masrik River basin and water sample points

in resulting solution was determined in a flame of by the AAS method (Havezov & Calev, 1983; Pupyshev, 2009).

Currently, there are a variety of modern methods for assessing the accumulation and transfer of chemical compounds in various components of environment. Analysis conducted to select the most appropriate method, as well as the possibility of adaptation and unification of the chosen method for our research, allowed us to dwell on the methods used by other scientists (Twining et al., 2004).

The accumulative coefficients were calculated using the following formulas:

$$Kd = C_2 \cdot V / C_1 \cdot M, \quad (1)$$

where C_1 – the amount of trace element in the soil; C_2 – the amount of trace element in the soil solution; V – the volume of the soil solution; M – the mass of the soil sample.

$$TF = B_1 / B_2, \quad (2)$$

where B_1 – the amount of microcomponent in the plant, B_2 – the amount of microcomponent in the soil.

Results

During the study period, the content of heavy metals in the water of rivers was studied according to nine sampling points (Table 1). The results of the analysis of the content of trace elements in the water of the rivers confirm the observed pattern of the prevalence of summer copper concentrations over spring, which is associated with the difference in water flow in the river, when summer low water is characterized by a sharp decrease in the water content of the rivers. Lead is characterized by the predominance of spring concentrations in the upper reaches of the Sotk river and summer concentrations

in the lower reaches of the Masrik river basin (Table 2). This trend can be justified by a sharp washout of storm drains in spring in the Sotk river basin and characterize by steep banks and accumulation in the summer period in the flat part of the Masrik river. In general, for both seasons, zinc and nickel differ in relatively high concentrations.

The distribution and transfer of heavy metals (HM) in the “soil–plants” system in the Masrik river basin with the Sotk tributary were also investigated (Table 3 and 4).

The calculation of the distribution coefficient of heavy metals in the soil was based on the data presented in Tables 1 and 3. According to the conducted research, the values of the distribution coefficient of heavy metals in soils depend on the pH level. The distribution coefficients increase with a decrease in the acidity values. Among the considered highest coefficients stood out Pb, and the minimum values were characteristic for Cu. Such values of the distribution coefficient indicate that copper has a high solubility and under favourable conditions, passes into the soil solution. High lead coefficients indicate its low solubility and high adsorption in the soil.

Indicators of the transfer factor for plant samples collected in the floodplain part of the Sotk and Masrik rivers are given in Table 5.

Plant communities are sensitive to technogenic exposure, and therefore can serve as indicators. As for the assessment of the transfer factor TF, the bioavailability of heavy metals for the studied plants was different. There are tendencies of high biological availability for copper and manganese for the bent growing in the Sotk river basin. Zinc and lead occupy an intermediate position, while minimum availability is characteristic for nickel. Investi-

Table 1. The content of trace elements in floodplain soils in the catchment areas of the Sotk and Masrik rivers, %/100 g of sample

№	Element	Numbers of soil samples					
		2		4		8	
		Date of sampling					
		05.2013	08.2013	05.2013	08.2013	05.2013	08.2013
1	Cu	0.0018	0.004	0.018	0.003	0.0018	0.005
2	Zn	0.018	0.03	0.0032	0.003	-	0.005
3	Ni	0.056	0.1	0.13	0.17	0.024	0.1
4	Pb	0.075	0.02	0.056	0.025	0.056	0.005
5	Co	0.0032	0.042	0.0075	0.042	-	0.04
6	Mn	0.042	0.073	0.18	0.11	0.018	0.05
7	Cd	0.02	0.04	-	0.041	-	0.04

Table 2. The content of trace elements in the waters of the Masrik River and its several tributaries, mg/l

Element	Sampling point																	
	1		2		3		4		5		6		7		8		9	
	Date of sampling																	
	05.13	08.13	05.13	08.13	05.13	08.13	05.13	08.13	05.13	08.13	05.13	08.13	05.13	08.13	05.13	08.13	05.13	08.13
	Sampling station																	
	Sotk River, at the gold factory	Sotk River, 1.5 km after the factory	Sotk River, after the factory, the first bridge	Sotk River, agricultural area	left tributary of the Masrik River – Aziz, under the bridge	Masrik River, near the village of Shatvan	Masrik River, not far from the village of Metz Masrik	Masrik River, before the Gilly Bridge	Masrik River, after the Gilly Bridge									
Cu ²⁺	0.00038	-	0.0004	0.006	0.00038	0.00067	0.00038	0.0007	0.0006	-	0.0007	0.00096	0.0007	0.0007	0.00065	0.0008	0.0007	0.0007
Zn ²⁺	0.0004	-	0.002	-	0.0004	-	0.0004	-	0.0005	-	0.0004	0.00015	0.01	-	0.001	-	0.005	-
Pb	0.0006	-	0.0006	0.0005	0.00054	0.0005	0.0007	0.0006	0.0005	-	0.0005	0.0006	0.00054	0.0004	0.00045	0.0006	0.0005	0.0009
Cd ²⁺	0.00015	-	0.0002	-	0.0001	0.0001	0.0001	-	0.0001	-	0.0001	-	0.0001	0.0002	0.00015	0.0002	0.0002	0.0001
Ni ²⁺	0.01	-	0.015	-	0.007	-	0.003	-	-	-	-	-	-	-	0.005	-	0.003	-

Table 3. The content of trace elements in the soil solution of the catchment of the Sotk and Masrik rivers, mg/100 g of soil

Element	Sampling point		
	2 (soil)	4 (soil)	8(soil)
Cu	0.0014	0.0005	0.0043
Pb	0.0004	0.0007	0.00025
Ni	0.007	0.007	0.007

Table 4. Distribution coefficients of microelements in the soils of the catchment area of the Sotk and Masrik rivers

Element	<i>Kd</i>		
	2(soil)	4 (soil)	8(soil)
Cu	1,8	5,0	0,16
Pb	49,0	34,0	19,0
Ni	13,2	23,2	13,2

Table 5. Transfer factor indicators for plants in points 2 (Sotk river) and 8 (Masrik river)

Plant	Sampling point	Transfer factor						
		Cu	Zn	Pb	Mn	Ni	Co	Cd
Bentgrass (<i>Agrostismarschalliana</i>)	2	0,44	0,11	0,11	0,66	0,001	0,06	0,025
Catabrosa (<i>Catabrosaaquatica</i>)	8	0,08	0,4	0,16	0,5	0,002	0,005	0,012

gations of the heavy metals accumulation by the water carrier in the Masrik river basin showed relatively high bioavailability of zinc and manganese, while lead and copper showed intermediate activity. Nickel and cobalt were distinguished by minimal transfer to the plant.

Discussion

A comparative analysis of the geochemical quality of the floodplain soils of the Sotk and Masrik rivers demonstrates trends in the all considered trace elements prevalence in the Sotk river catchment soils over the second in the spring season. It can be explained with the mining impact in the Sotk river basin through the flushing of spring slope drains from the headwaters to the floodplain.

Some studies (Popova, 2016) emphasize that the ecosystem located in the zone of direct anthropogenic impact is more depressed than remote areas of impact. It was confirmed by the results of the transfer of heavy metals from soil to plants. Thus the coefficient of biological absorption in this study was used in the same way as in our studies as the main indicator for determining the anthropogenic level of contamination of test phytocenoses and monitoring. The results of the study (Szabó et al., 2008) revealed that the indication of plants can be the main driving force of environmental studies to recognize the unusual features of soil attributes. Soil samples from Central Spish (Takáč et al., 2009) contained high proportions of mobile forms, which correspond to the following sequence: Pb> Zn> Cu. The accumulated forms were characterized by their sequence: Cu> Zn> Pb. A certain sequence has emerged among the priority heavy metals: for mobile forms – Ni> Cu> Pb and for the deposited forms – Ni> Pb> Cu.

Soil pH is one of the parameters that significantly affect the proportion of bio available metal forms. Membrane transfer of heavy metals leads to an increase in the level of metals in plants through the availability of concentrations of soil solution (Cataldo & Wildung, 1978). This case study of metal accumulation in plants confirm their use as indicators in the environment detecting changes. The authors studied the behaviour of Cd, Ti and Ni. It would seem that metals may exhibit similar trends. However, as studies have shown, the assimilation of metals by plants is not always proportional to their concentrations in the soil solution, which is confirmed by our research. For example, despite the relatively high nickel content in the soil solution, its transfer to plants turned out to be at the lowest level in comparison with other metals. Plants probably have

certain protective mechanisms which assist to minimize the risk of heavy metals transfer to the food (Komal et al., 2014).

Research results in Nepal (Yan et al., 2014) showed that Cu, Zn, and Pb concentrations in soil samples are significantly higher than in grass samples, which is consistent with our research. Calculation of the transfer factor confirmed that the distribution of the biological ability of the absorption of heavy metals from soil by grass corresponds to a certain sequence Zn> Cu> Pb. This is partly consistent with our research.

Conclusion

Studies assessing the mobility of a number of microcomponents in the soil and in the “soil–plant” system in the catchment basin of the Masrik river including the Sotk river as the main tributary, made it possible to identify the characteristic patterns of the behaviour of heavy metals. Analysis of trends and patterns revealed the presence of a high level of solubility of copper in the soil, as well as the significant bioavailability of this metal by plants. The tendencies of low solubility in soil for lead have been found. But on the issue of bioavailability by plants, Pb exhibits intermediate behaviour. Nickel exhibits the lowest chemical activity both in the soil and when transferred to plants. It was established that there are some differences between the behaviour of trace elements in floodplain soils of the Sotk and Masrik river basins. The obtained data can be used to predict the dynamics of plant populations and communities in polluted territories and monitor the state of natural ecosystems.

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