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MIGRATION OF COPPER IN WATER–SEDIMENT SYSTEM

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In the paper the migration of copper in water–sediment system and the dependence between copper content and pH, and dissolved oxygen were investigated. The Hrazdan River was the study area, one of the largest and the most important rivers in Armenia. Samples were taken from 6 sampling points of the Hrazdan River basin (66 samples of water and bottom sediment) during 2012–2013. Results of copper content analysis reveal that none of the identified values exceed maximum permissible concentration. The correlation coefficients between copper content and, both for pH and dissolved oxygen, were obtained. The influence of pH and dissolved oxygen on migration of copper in water–bottom sediment system was identified.

***Keywords*:** bottom sediment, copper, correlation coefficients, Hrazdan River.

Introduction. Although metals and their compounds are the components of natural ecosystem, but contamination of water, soil, bottom sediment by heavy metals is a serious environmental problem. Heavy metals are accumulated in the bottom sediment due to different physical and chemical adsorption mechanisms. However, depending on conditions (changes in pH, redox potential, organic matter content) the secondary pollution can occur [1].

Accumulation of heavy metals in the sediments on the one hand promotes self-cleaning of the reservoir, and, on the other hand, there is danger of contaminating sediments with heavy metals. It is dangerous, because the sediments are the habitat for benthic organisms and the substrate for aquatic plants, which in turn are food for fish. It is obvious that the accumulation of heavy metals in sediment does not prevent the danger of accumulation of heavy metals in the food chain and ultimately influence on human health [2].

Copper is one of the most important elements for living organisms. It is contained in many enzymes. The deficiency of copper in the organism can cause abnormalities in the synthesis of proteins, vitamins and lipids. It is essential for all organisms. However, the excessive amount can cause large copper toxicity in all types of living organisms [3]. MPC for copper in the aquatic environment is 2 *mg*/*L* [4].

Materials and Methods. Study area: the Hrazdan River starts from the Lake Sevan, flowing through the central regions of the country and also through

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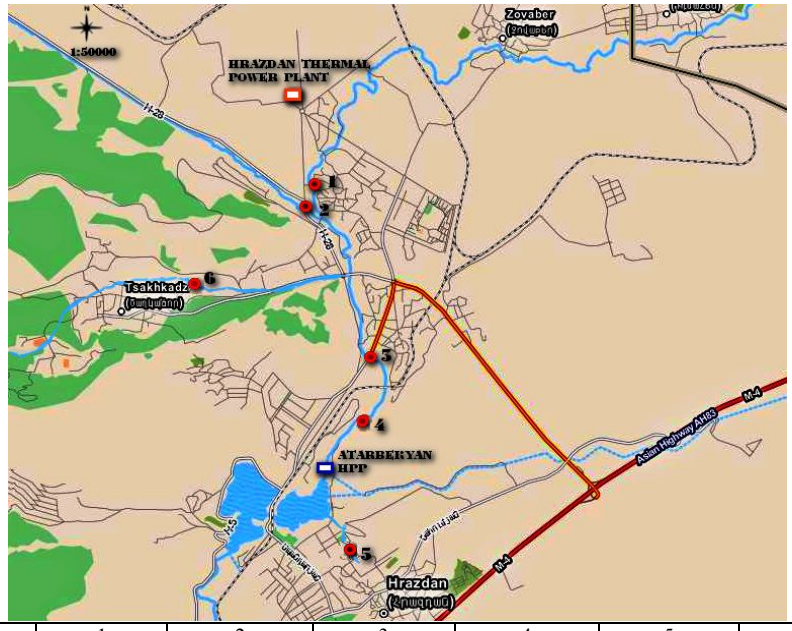
the Capital City. It is considered to be the main water vein of Armenia. The river is fully used in Sevan–Hrazdan water–economical complex for irrigation and energy purposes, as well as for water supply, recreation. The lenght of the river is 141 *km*, basin area is 2560 km^2 without the Lake Sevan [5].

33 sediment samples and 33 surface water samples were collected from 6 sampling points along the Hrazdan River (Fig. 1).



	1	2	3	4	5	6
Coordinates (NA, EL)	40°32'52.5", 44°45'19.8"	40°32'43.3", 44°45'16.5"	40°31'32.5", 44°45'55.0"	40°31'04.4", 44°45'53.5"	40°29'59.6", 44°45'53.5"	40°29'45.7", 44°44'09.2"
Absolute height, *m*	1720	1714	1710	1708	1695	1690

Fig. 1. Locations of studied sampling points of Hrazdan River basin with detailed descriptions of the sampling points.

For determining copper concentration inductively coupled plasma mass spectrometer ELAN 9000 (“Perkin Elmer”, US) was used [6]. For bottom sediment (BS) samples preparation Berghoff MWS 3+microwave digestion equipment in accordance with 3052 method of USEPA [7] was used. pH and dissolved oxygen (DO) were determined by the YSI 556 MPS equipment [8].

In order to evaluate the influence of pH and DO on migration of copper within water–BS system the linear dependence of ratio of copper content in water and BS with DO and pH was investigated. The correlation coefficient was determined by formulas from [9]:

$$S_{xx} = \sum x^2 - \left(\sum x\right)^2 / n, \quad S_{yy} = \sum y^2 - \left(\sum y\right)^2 / n,$$
$$S_{xy} = \sum xy - \left(\sum x\right)\left(\sum y\right) / n, \quad R = S_{xy} / \sqrt{S_{xx} S_{yy}}.$$

Results and Discussion. In Table the content of copper both in water and in sediment samples, taken from the Hrazdan River basin is given.

Content of cupper, dissolved oxygen and pH values in the sampling points of the Hrazdan River

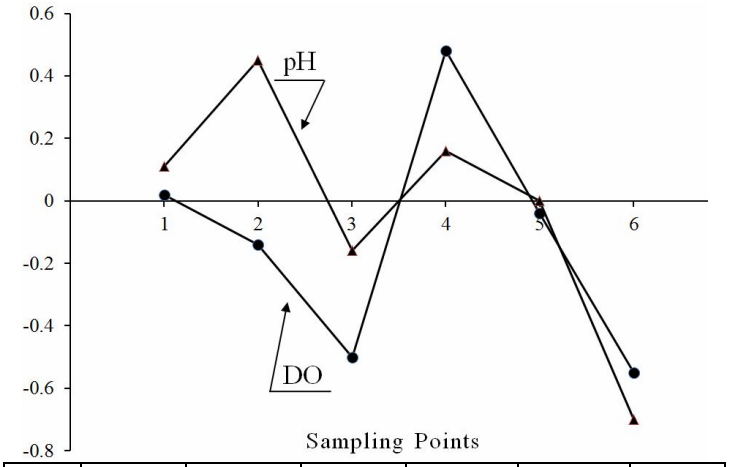
№	Date	DO	pH	$[Cu]_{H_2O}$, *mg/L*	$[Cu]_{BS}$, *g/kg*	$[Cu]_{H_2O}/[Cu]_{BS}$
1	07.2012	6.65	7.74	0.00009	0.0525	0.00170
	08.2012	8.89	8.08	0.0158	0.0290	0.54410
	09.2012	5.57	8.23	0.0031	0.0497	0.06240
	02.2013	13.48	8.42	0.0026	0.0430	0.06010
	05.2013	7.53	8.00	0.0015	0.0565	0.02650
	07.2013	11.78	8.02	0.0010	0.0351	0.02740
2	07.2012	8.96	7.81	0.0012	0.0259	0.04710
	08.2012	9.75	8.54	0.0051	0.0499	0.10290
	09.2012	6.37	8.76	0.0016	0.0308	0.05310
	02.2013	13.77	8.54	0.0020	0.0471	0.04230
	05.2013	8.26	7.40	0.0013	0.0411	0.03270
	07.2013	11.08	8.20	0.0012	0.0520	0.02320
3	07.2012	8.56	7.08	0.0019	0.0325	0.05683
	08.2012	14.74	7.90	0.0018	0.0483	0.03662
	09.2012	9.77	8.28	0.0018	0.0448	0.04121
	07.2013	10.12	8.00	0.0012	0.0155	0.07971
4	07.2012	9.30	8.22	0.0011	0.0507	0.02230
	08.2012	12.50	8.15	0.0025	0.0245	0.10090
	09.2012	10.76	8.19	0.0019	0.0212	0.09030
	05.2013	8.48	5.90	0.0011	0.0343	0.03160
	07.2013	11.52	7.80	0.0037	0.0066	0.55200
5	07.2012	8.02	8.92	0.0016	0.0277	0.05590
	08.2012	10.12	8.59	0.0015	0.0250	0.05870
	09.2012	8.98	8.61	0.0017	0.0294	0.05870
	02.2013	15.20	8.52	0.0025	0.0265	0.09360
	05.2013	8.01	7.70	0.0012	0.0356	0.03400
	07.2013	9.02	8.40	0.0013	0.0029	0.44550
6	07.2012	–	8.26	0.0050	0.0611	0.08210
	08.2012	4.25	7.94	0.0013	0.0462	0.02910
	09.2012	6.25	8.12	0.0008	0.0347	0.02310
	02.2013	7.69	7.99	0.0019	0.0559	0.03410
	05.2013	1.91	7.70	0.0011	0.0301	0.03630
	07.2013	1.89	7.50	0.0023	0.0027	0.84740

The influence of pH and DO on migration of copper in 1st sampling point lead to the transfer of BS to water. But the DO has a very little influence on migration of copper. In 2nd sampling point the influences of pH and DO are different: for DO it is from water to BS, but for pH it is from BS to water. pH and DO have an influence on migration of copper in 3rd sampling point and the migration is from water to BS. In 4th sampling point pH and DO effect on migration of copper and the migration is from BS to water. In 5th sampling point pH and DO effect on migration of copper and the migration is from water to BS, but the effects are insignificant. pH and DO effect on migration of copper in 6th sampling point and the migration is from water to BS.

In Fig. 2 it is shown graphically, that the influanes of pH values and DO on migraton of copper are mostly synergistic.

As we can see in all points except the 2nd sampling point the correlation coefficients are changing similarly, only in the 2nd sampling point the influences of DO and pH values have different character.

In Fig. 2 are presented the obtained correlation coefficients.



№	1	2	3	4	5	6
DO	0.012589	–0.13892	–0.50024	0.475005	–0.04659	–0.54623
pH	0.10823	0.444505	–0.15776	0.156022	–0.0071	–0.71297

Fig. 2. Correlation coefficients between ratio of copper content in water and bottom sediment, dissolved oxygen and pH.

Conclusion. From the obtained results we can conclude that DO and pH have influence on migration of copper in the water–BS system. The influence of DO on migration of copper is mostly significant in 3rd, 4th and 6th sampling points. And the influence of pH on migration of copper is mostly significant in 2nd and 6th sampling points. DO and pH effect on migration of copper is very similar, only in 2nd sampling point their effects are different.

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