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AGRICULTURAL RISK ASSESSMENT OF THE HEAVY METAL AND MINERAL SALT POLLUTION OF RIVER ECOSYSTEMS IN THE VOGHJI RIVER CATCHMENT AREA, ARMENIA

G.A. GEVORGYAN[1], V.M. VARAGYAN[2], A.L. VARAGYAN[2]

[1] Institute of Hydroecology and Ichthyology of Scientific Center of Zoology and Hydroecology of NAS RA, [2]Chair of Ecology and Nature Protection of Faculty of Biology of YSU
gev_gor@mail.ru

The irrigation properties of the Voghji and its main tributaries – Artsvanik and Geghi rivers and their agricultural risks according to the content of some heavy metals and dissolved mineral salts were investigated. Water sampling was implemented in irrigation period (July) of 2016. The results of the study showed that waters in the Voghji river site located in the downstream from Kapan town and in the area of the Artsvanik river mouth, according to molybdenum, manganese, iron and sulfate contents, were unallowable for the use for irrigation purpose and may pose agricultural risks.

Voghji river catchment basin – dissolved mineral salts – heavy metals – irrigation properties – agricultural risks

Ուսումնասիրվել են Ողջի և նրա հիմնական վտակներ՝ Արծվանիկ ու Գեղի գետերի ոռոգիչ հատկությունները և դրանց գյուղատնտեսական ռիսկերը ըստ որոշ ծանր մետաղների ու լուծված հանքային աղերի պարունակության: Ջրերի նմուշառումն իրականացվել է 2016 թ. ոռոգման շրջանում (հուլիս): Հետազոտության արդյունքները ցույց են տվել, որ Ողջի գետի Կապան քաղաքից ներքև ընկած և Արծվանիկ գետի գետաբերանային հատվածի ջրերը, ըստ մոլիբդենի, մանգանի, երկաթի և սուլֆատի պարունակության, անթույլատրելի են եղել ոռոգման նպատակով օգտագործման համար և կարող են առաջացնել գյուղատնտեսական ռիսկեր:

Ողջի գետի ջրահավաք ավազան – լուծված հանքային աղեր – ծանր մետաղներ – ոռոգիչ հատկություններ – գյուղատնտեսական ռիսկեր

Изучены ирригационные свойства реки Вохчи и ее основных притоков – Арцваник и Гехи, и их сельскохозяйственных рисков, по содержанию некоторых тяжелых металлов и растворенных минеральных солей. Отбор проб воды осуществлялся в поливной период (июль) 2016 года. Результаты исследования показали, что воды в участке реки Вохчи расположенной ниже города Капан и в устье реки Арцваник, по содержанию молибдена, марганца, железа и сульфата, были недопустимы для использования оросительных целей и могут создавать сельскохозяйственные риски.

Водосборный бассейн реки Вохчи – растворенные минеральные соли – тяжелые металлы – ирригационные свойства – сельскохозяйственные риски

Water, as it's known, is a base of all the processes occurring on the Earth. It's also required in all the spheres of human economic activities. Irrigation water has also high importance. Incorrect irrigation may cause the secondary salinisation, swamping and technogenic matter pollution of the significant part of irrigated soils, as a results of which, they become unallowable for use for agricultural purpose.

In many countries (USA, Germany, Czech Republic, etc.), the issues of the assessment, monitoring and management of irrigation waters are under the governmental control [18].

The irrigation properties of waters in the Republic of Armenia (RA) are slightly studied, whereas the necessity for solving these problems is highlighted by the fact that existing water resources are permanently exposed to pollution, as a result, they obtain new irrigation properties [13, 18].

Surface waters in the Voghji river catchment area are mainly used for irrigation and energetic purposes [17]. The results of our previous investigations showed that river ecosystems in this area are under the impact of such anthropogenic factors as mining industrial and household activities [3–5, 14, 15, 19, 20]. Due to the insufficient management of anthropogenic discharges in the Voghji river catchment area, the pollution of aquatic ecosystems may become the reason of the deterioration of the irrigation properties of waters. Therefore, by performing hydrochemical investigation in the risky sites of the Voghji river catchment area, it's possible to characterize the water irrigation properties and their possible agricultural risks.

The aim of the present study was to assess the agricultural risks of the heavy metal and dissolved mineral salt pollution of the river ecosystems in the Voghji river catchment area.

Materials and methods. The Voghji (length – 82 km), Geghi (length – 30 km) and Artsvanik (length – 17 km) rivers in the Voghji river catchment area were investigated. The Voghji river catchment area is situated in the south of the RA and includes the southern part of Syunik Marz/Province in the territory of the RA. The surface area of the river catchment basin is 1175 km^2 (933 km^2 in the territory of the RA). The rivers in the area are mainly short, fast flowing, shallow and belong to the catchment basin of the transboundary Araks river [17].

The investigations were conducted in 2016. Samples for hydrochemical analysis were taken in irrigation period, in July (tab.1).

Table 1. Coordinates of the rivers investigated sites in the Voghji river catchment basin under investigation

Sampling site number	N/Lat	E/Long	River site location
1	39°09'21.7"	46°07'59.0"	Voghji river site located about 2.0 km upstream from Kajaran town
2	39°09'01.8"	46°11'34.3"	Voghji river site located about 3.2 km downstream from Kajaran town
3	39°13'27.7"	46°20'19.4"	Voghji river site located about 6.0 km upstream from Kapan town
4	39°11'52.5"	46°28'05.4"	Voghji river site located about 5.4 km downstream from Kapan town
5	39°11'55.0"	46°28'05.2"	Artsvanik river mouth
6	39°11'58.7"	46°15'32.8"	Geghi river mouth

Electrical conductivity (EC) values in the river waters were measured by "HI98129" multi-parameter analyzer.

The contents of calcium (oxalate method), magnesium (calmagite method), potassium (turbidimetric tetraphenylborate method), sulfate (turbidimetric method), copper (bicinchoninate method), molybdenum (mercaptoacetic acid method) ions as well as iron (phenanthroline method), zinc (zincon method) and manganese (PAN method) elements were determined by "HI83200" multiparameter photometer [6]. Chloride ion content was determined by the silvermetric method, and the concentrations of carbonate and hydrocarbonate ions – by the titrimetric methods [21]. Prior to the molybdenum ion measurements, the water samples were evaporated to increase the density of the metal in the water, which made it possible to increase the sensitivity of the metal measurements. Due to the limited sulfate ion measurement range of the photometer, the water samples in some cases were diluted to decrease the density of sulfates in the water.

The agricultural risks of river water pollution were assessed by comparing the registered values of the parameters to the surface water quality norms accepted in the RA, as well as by the residual sodium carbonate (RSC) index and the magnesium adsorption ratio (MAR) [1, 12, 16].

Individual heavy metal pollution degree for river water use for irrigation purpose was assessed by the pollution index (PI) [11].

Integrated heavy metal pollution degree for river water use for irrigation purpose was evaluated by the Nemerow and Sumitomo's water pollution index (NSWPI) [7].

Results and Discussion. The values of some heavy metals (HM) and dissolved mineral salts (DMS) contents, RSC index, MAR and EC in the river ecosystems of the Voghji river catchment basin are presented in tab. 2.

Table 2. Some HM, DMS (mg/l) contents, RSC index (meq/l), MAR (%) and EC (mS/cm) values in the waters of the Voghji, Artsvanik and Geghi rivers.

Parameter	Observation site number					
	1	**2**	**3**	**4**	**5**	**6**
Ca^{2+}	20.0	35.0	35.0	50.0	85.0	30.0
BL	18.3				22.8	
MPC	300.0					
Mg^{2+}	5.0	10.0	5.0	10.0	10.0	5.0
BL	4.8				4.4	
MPC	200.0					
K^{+}	1.50	2.50	1.50	5.00	8.50	1.50
BL	1.45				1.12	
MPC	11.62				8.96	
Cl^{-}	0.70	1.27	5.64	2.22	12.42	5.81
BL	6.00				3.53	
MPC	200.00					
SO_4^{2-}	25.00	45.00	30.00	180.00	375.00	25.00
BL	26.72				16.00	
MPC	250.00					
HCO_3^{-}	94.3	146.7	154.0	151.5	131.4	142.6
BL	-					
MPC	-					
CO_3^{2-}	absent					
BL	-					
MPC	-					
RSC	0.14	-0.16	0.37	-0.83	-2.91	0.43
MPC	2.50					
MAR	29.2	32.0	19.0	24.8	16.2	21.5
SL*	50.0					
EC	90.0	127.0	186.0	496.0	670.0	152.0
BL	168.5					182.6
MPC	1500.0					

Parameter	1	2	3	4	5	6
Cu^{2+}	0.006	0.019	0.017	0.094	0.043	0.003
BL**	0.004				0.002	
MPC***	0.100					
Mo^{6+}	0.007	0.046	0.043	0.137	0.161	0.008
BL**	0.015				0.007	
MPC***	0.120				0.056	
Mn	0.004	0.017	0.010	0.172	0.166	0.008
BL	0.004				0.005	
MPC	0.032				0.040	
Fe	0.290	0.550	0.570	6.880	9.340	0.120
BL	0.031				0.063	
MPC	1.000					
Zn	0.040	0.060	0.050	0.090	0.100	0.020
BL	0.003				0.001	
MPC	0.500					

* safety level
** BL of the total content of the element
*** MPC of the total content of the element

The results of the study showed that DMS and HM contents in the investigated river waters were conditioned by both natural and anthropogenic sources, as the concentrations of different DMS ans HM in all the observation sites exceeded the background level (BL), which confirmed the existence of anthropogenic pressure on the river ecosystems (tab. 2). Tab. 2 shows that comparatively high concentrations of HM and DMS were registered in the observation sites located in the downstream from Kajaran, Kapan towns and Artsvanik tailing dump (Nos 2 – 5), which were probably conditioned by the impact of urban and mining industrial discharges.

According to DMS (Ca^{2+}, Mg^{2+}, K^{+}, Cl^{-}, HCO_3^{-} and CO_3^{2-}) content, RSC index, MAR and EC values, the river waters in all the investigated observation sites were allowable for use for irrigation purpose. Only the Artsvanik river waters in the investigated observation site (No 5), according to sulfate ion content, were unallowable for use for irrigation purpose. In this observation site, sulfate ion content exceeded the maximum permissible concentration (MPC) for water use for irrigation purpose by 1.5 times (tab. 2). Although sulfate ion is one of components composing total DMS content in irrigation waters and has high importance for increasing the productivity of crops, however the unallowable content of sulfate ion in irrigation waters may negatively affect the growth of plants growing on soils irrigated by these waters and can cause a decrease in phosphorus availability for plants [8].

According to HM content, the river waters in the observation sites Nos 4 and 5 were unallowable for use for irrigation purpose, as molybdenum content exceeded the MPC for water use for irrigation purpose by 1.1 and 1.3 times respectively, manganese content – by 5.4 and 5.2 times respectively, and iron content – by 6.9 and 9.4 times respectively (tab. 2). In these river sites, the river waters for the use for irrigation purpose were estimated as “potentially polluted” according to molybdenum content and “heavily polluted” according to manganese, iron, as well as integrated HM contents. From the point of view of HM content, the river waters in other observation sites were assessed as “non-polluted” for use for irrigation purpose (tab. 3).

Irrigation waters with high molybdenum content may cause the pollution of soils and vegetation growing on them and toxically affect livestock through forage [2]. High concentrations of manganese in irrigation waters can toxically affect crops causing the swelling of cell walls, the withering of leafs and brown spots on leaves [2, 9, 10]. In

case of irrigation with waters having the unallowable content of iron, soil acidification and the loss of essential phosphorus and molybdenum may occur [2].

Table 3. HM pollution degree (for water use for irrigation purpose) in the Voghji, Artsvanik and Geghi rivers

Observation site number	PI_{Cu}	PD	PI_{Mo}	PD	PI_{Mn}	PD	PI_{Fe}	PD	PI_{Zn}	PD	NSWPI	PD
1	0.1	NP	0.1	NP	0.1	NP	0.3	NP	0.1	NP	0.2	NP
2	0.2		0.4		0.5		0.5		0.1		0.4	
3	0.2		0.4		0.3		0.5		0.1		0.4	
4	0.9		1.1	PP	5.2	HP	6.3	HP	0.2		4.8	HP
5	0.4		1.3		5.0		8.5		0.2		6.4	
6	<0.1		0.1	NP	0.2	NP	0.1	NP	<0.1		0.2	NP

Although from the point of view of DMS (Ca^{2+}, Mg^{2+}, K^{+}, Cl^{-}, HCO_3^{-} and CO_3^{2-}) content, RSC index, MAR and EC values, the investigated river waters were allowable for use for irrigation purpose, however in case of individual salts, particularly sulfate ion content, the irrigation waters of the Artsvanik river can pose agricultural risks.

Some HM (Mo^{6+}, Mn and Fe) contents in the Voghji river site located in the downstream from Kapan town and in the mouth area of the Artsvanik river were risky for water use for irrigation purpose and may cause the loss of crop productivity and livestock production.

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