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ASSESSMENT OF SELF-PURIFICATION CHEMICAL PROCESSES OF THE RIVER HRAZDAN IN ARMENIA

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In this study the chemical self-purification processes were investigated based on the changes in the concentration of dissolved oxygen and organic compounds in the form of 5-day biochemical oxygen demand (BOD_5). The correlation between the dissolved oxygen, BOD_5, ammonium nitrogen, nitrate nitrogen was assessed for the downstream of the Hrazdan River. It has been identified that the Hrazdan River has a high level of self-purification capacity. Due to natural chemical processes,, in the river water the amount of organic pollutants is reduced by about 2-10 times, and the content of dissolved oxygen is recovered by up to 25 times in 13 km of the river part.

Fig. 1, table 1, ref. 13.

Introduction. One of the significant capacities of the ecosystems is their ability to reduce the amount of contaminants discharged to the water body through inter-chemical biological and physical processes. The further behavior of organic compounds discharged to natural waters depends not only on their reactivity, physicochemical and biological factors, but also on the characteristics of the water ecosystem, such as the pH, redox reaction, concentration of dissolved oxygen (DO), temperature, and so on. Natural water systems have reserves and the ability to regulate or absorb additional amounts of pollutants. This ability is called self-purification capacity or buffer capacity of a water body [1-4].

In the process of self-purification within rivers, more importance is given to the chemical processes, which differ from physical and biological types by the variety of processes, at the same time by the possibility to be measured [3]. The concentration of dissolved oxygen is considered to be a direct factor for chemical processes taking place in water body. Oxygen, as an oxidant, in the form of both molecular and radicals, participates in the decomposition reactions of organic contaminants in a water body, oxidation

reactions, abiotic catalytic and photochemical processes occurring by the formation of reactive particles [4].

The intensity and efficiency of self-purification chemical processes can be assessed by the absolute values of the concentrations of DO in a water body [3-4].

There are several studies conducted to assess the self-purification capacities of rivers in Armenia [5-6]. Rivers in Armenia are mountainous, fast flowing, of medium to small size. Due to the peculiarities of large mountain slopes, riverbeds, climatic conditions, as well as vast fluctuations in river flow during a year, rivers in the country are characterized by the ability to absorb a sufficient amount of oxygen, which ensures the intensity of oxidation processes in a water body [7]. This shows that the rivers in the country have a high ability to be self-purified. However, there are a few if any investigations to clearly describe the behavior of organic compounds discharged to a river and their correlation between the content of dissolved oxygen in the water of rivers in Armenia [5].

For this purpose, this study aims to investigate self-purification chemical processes by assessing the correlation between DO, 5-day biochemical oxygen demand (BOD_5), and nutrient changes. The results will help assess the overall ability of the Hrazdan River to reduce organic pollution and find the pressure threshold.

This study should allow to deeply understanding the actual ecological state of the Hrazdan River, to assess the anthropogenic pressure by organic pollution and their consequences, as well as estimate the changes in ecological conditions within the water body.

Study of area. The efficiency of self-purification chemical processes was assessed in the downstream Hrazdan River. The Hrazdan River is one of the largest and most abundant left tributaries of the Araks River. The length of the river is 141 *km*, catchment area – 7310 km^2 (without the Lake Sevan basin - 2560 km^2). The average annual runoff is 0.71 km^3 [8]. The source of the river is considered to be a canal that diverts water from Lake Sevan to the underground Kanaker hydroelectric power station (as a result of the creation of the Sevan-Hrazdan hydropower-irrigation complex). The river flows in a bound bed through a densely populated area, and, irrigating the fields of the Ararat valley, flows into the Araks River. The city of Yerevan, the capital of the Republic of Armenia, is located on the lower reaches of the Hrazdan [8]. The urban wastewater of the city discharged in the river is not adequately treated and pollutes the river by high level of organic compounds and nutrients [9].

Materials and research methods. The research study was conducted for two points at the Hrazdan River, located as follows: №55 – 6 *km* below the city of Yerevan, near the village of Darbnik, №56 – at the mouth of the river. The length between the sampling points was around

13 *km*. The assessment was conducted each month in 2018-2020. The water samples were taken in accordance with ISO 5661 requirements [10]. In the water samples dissolved oxygen, pH and BOD_5, ammonium and nitrate nitrogen were analyzed. HACH Portable pH, Conductivity/TDS Dissolved Oxygen Meter was used to measure pH and dissolved oxygen in water samples [11]. Determination of ammonium and nitrate ions was carried out by spectrophotometric method, using Griess and Nessler's reagents, accordingly [12-13]. BOD_5 was determined by the test tube method at a temperature of 20 ± 1°C. BOD_5 was measured as an indicator of the content of easily degradable organic pollutants in a water body [13].

Results and Discussion. According to the water analyses data, the monthly and annual changes in the concentration of DO were identified for two points in the Hrazdan River: near discharging partly treated urban wastewater into the River (sampling point №55) and 13 *km* after this discharge, at the river mouth (sampling point №56). The data show that in both sampling points the relatively high oxygen content is observed during the flooding of the river (spring, then autumn), when the river flow is quite large and the degree of water aeration is increased (Table 1).

During spring months (April-May), the content of BOD_5 in the river water decreased up to 6-10 *times* in the 13 *km* downstream. Due to the relatively high content of DO in water, the oxidation of the ammonium ion into nitrates also passed intensively. The concentration of ammonium nitrogen in the sampling point №56 decreased by 7-10 *times* compared to the sampling point №55. As a result of this oxidation, the nitrate content in the water, on the contrary, increased relatively by about 2-3 *times* (Table 1).

The minimum content of DO was observed during summer times, due to high air and water temperature, minimum river flow and very low water aeration. In summer, with the same level of wastewater discharge, the content of organic compounds and ammonium ions is maximum.

Fig. 2 shows a direct link between DO concentration and decrease of BOD_5 and ammonium nitrogen for 13 *km* river section, downstream the Harzdan River. It was identified that during three years of observations the self-purification capacity of the river decreased 2.5 *times* both for BOD_5 and $N\text{-}NH_4^+$ (correlation ratio decreased from 19 to 8 and from 27 to 11 in 2018-2020, accordingly), and no significant changes were recorded for $N\text{-}NO_3^-$ (correlation ratio was constantly 2 in 2018-2020).

Table 1

Change of several hydro-chemical parameters for the Hrazdan River

Parameter	2018		2019		2020	
	№55	№56	№55	№56	№55	№56
DO, *mg/l*						
maximum conc.	7.60	8.63	8.54	8.47	9.47	11.02
minimum conc.	0.16	4.01	0.08	2.06	0.18	2.36
average conc.	2.77	5.82	3.20	4.63	3.71	5.62
pH						
maximum conc.	7.74	8.26	7.95	8.32	8.10	8.00
minimum conc.	6.94	7.11	7.01	7.22	7.00	7.35
average conc.	7.51	7.66	7.45	7.68	7.56	7.71
BOD_5, *mg/l*						
maximum conc.	32.6	5.70	45.2	3.12	27.0	4.50
minimum conc.	3.05	1.06	2.52	1.35	1.30	1.50
average conc.	19.60	2.14	17.33	2.08	13.05	2.62
$N\text{-}NH_4^+$, *mg/l*						
maximum conc.	80.08	5.38	37.42	4.57	47.44	5.85
minimum conc.	1.95	0.25	4.54	0.92	6.06	1.18
average conc.	27.95	2.19	19.21	2.26	21.74	3.08
$N\text{-}NO_3^-$, *mg/l*						
maximum conc.	2.54	5.84	3.49	6.08	2.62	5.25
minimum conc.	0.07	2.27	0.07	2.48	0.06	2.40
average conc.	1.12	4.01	1.26	3.82	1.02	3.41

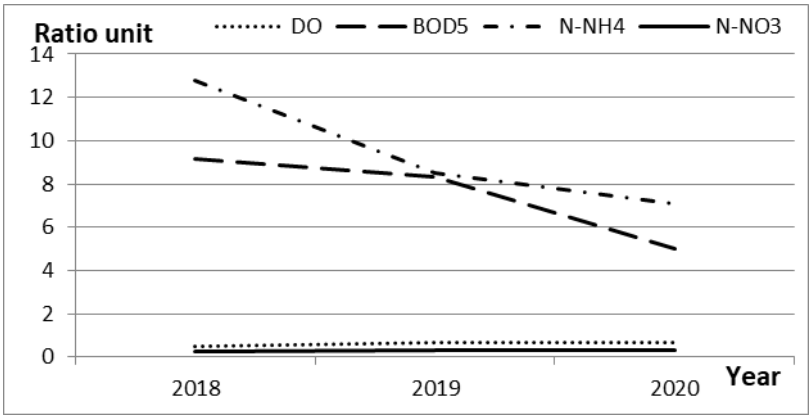

Fig. 2. Ratio of changes of hydro-chemical parameters in observation points №55 and №56.

Conclusion. It was shown that the high level of self-purification capacity for downstream flow of the Hrazdan River was due to the high ability to solve oxygen in water. As a result, the concentrations of organic pollutants and ammonium nitrogen have decreased up to 10 *times* in the 13 *km* section of the river. However, due to the continuous impact of partially

treated urban wastewater discharge, the self-purification capacity decreased 2.5 *times* in 2018-2020. Based on the findings of this study, water management agencies should contribute to minimizing by at least 2.5 *times* the impact of urban wastewater reducing the amount of BOD_5 and ammonium nitrogen in the wastewater discharge permits.

ОЦЕНКА ХИМИЧЕСКИХ ПРОЦЕССОВ САМООЧИЩЕНИЯ РЕКИ РАЗДАН В АРМЕНИИ

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В работе изучались процессы химического самоочищения водоема, на основе изменений концентраций растворенного кислорода и органических соединений в форме биохимического потребления кислорода за пять суток ($БПК_5$). Были оценены корреляции между растворенным кислородом, $БПК_5$, аммонийным азотом и нитратным азотом в воде в нижнем течении реки Раздан. Установлено, что река Раздан обладает высокой способностью к самоочищению. Благодаря естественным химическим процессам в речной воде количество органических загрязнителей снижается в 2-10 раз, а также содержание растворенного кислорода восстанавливается до 25 раз на расстоянии 13 *км* по течению вниз.

ՀՀ ՀՐԱԶԴԱՆ ԳԵՏԻ ԻՆՔՆԱՄԱՔՐՄԱՆ ՔԻՄԻԱԿԱՆ ԳՈՐԾԸՆԹԱՑՆԵՐԻ ԳՆԱՀԱՏՈՒՄ

Լ. Ա. ՄԱՐԳԱՐՅԱՆ, Ս. Ս. ՀԱՅՐԱՊԵՏՅԱՆ, Լ. Ս. ԲԱՆՅԱՆ և Ա. Ի. ՄԱՐՏԻՐՅԱՆ

Աշխատանքում ուսումնասիրվել են ջրային ռեսուրսում տեղի ունեցող ինքնամաքրման քիմիական գործընթացները՝ հիմնվելով լուծված թթվածնի և օրգանական միացությունների՝ արտահայտված թթվածնի կենսաքիմիական հնգօրյա պահանջով (ԹԿՊ5), պարունակությունների փոփոխության վրա: Գնահատվել է Հրազդան գետի ստորին հոսանքների ջրում լուծված թթվածնի, ԹԿՊ5-ի, ամոնիումային ազոտի և նիտրատային ազոտի միջև հարաբերակցությունները: Պարզվել է, որ Հրազդան գետն օժտված է ինքնամաքրման բարձր ընդունակությամբ: Գետի ջրերում բնական քիմիական պրոցեսների հաշվին օրգանական աղտոտիչների քանակը կրճատվում է 2-10 անգամ, իսկ ԼԹ-ի պարունակությունը վերականգնվում է մինչև 25 անգամ՝ գետի հոսքով դեպի ներքև 13 կմ հեռավորության վրա:

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