

## **SYSTEMIC-ENTROPY APPROACH FOR ESTIMATING THE WATER QUALITY OF A RIVER**

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### **ABSTRACT**

For the first time using the entropy water quality index, the degree of water pollution of the river Akhuryan and its tributaries Asotck and Karkachun was assessed. It was shown that from the source to the mouth of the river there is an increase in the value of the entropic water quality index and Armenian water quality index, which indicates the decline in the quality of water of the rivers from the 1st to the 4th class of pollution. After the cities of Amasia and Gyumri entropic water quality index and Armenian water quality index increase, indicating a decrease in water quality due to pollution of water in the river Akhuryan by domestic wastewaters. It has been shown for river Ashotsk that from the source to the river mouth there is an increase in the cost of entropic water quality index, however, water quality remains of the first class. For the river Karkachun water quality was of the second class. It was established that the entropic water quality index has a linear relationship with the Armenian water quality index, water contamination index and specific combinatory water quality index and an inverse relationship with the Canadian water quality index.

*Keywords:* river Akhuryan, entropy water quality index, Armenian water quality index, entropy, Armenia.

### **AIMS AND BACKGROUND**

Rivers are the most important natural resources for human development. The study of ecological status of the rivers in Armenia is important for evaluation of their water quality, as well as for their further rational use<sup>1</sup>. Water is a nonrenewable resource and unreasonable exploitation of it almost everywhere led to a decrease in water quality<sup>2</sup>. Water sources may be mainly in the form of rivers, lakes, glaciers, rain water, ground water, etc. Besides the need of water for drinking, water resources play a vital role

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in various sectors of economy such as industrial activities, hydropower generation, agriculture, forestry, fisheries and other creative activities. Urbanisation, industrialisation and other anthropogenic activities as well as some natural processes affect water resources badly. Unplanned resource consumption finally will become threat to the water ecosystem<sup>3-6</sup>. The comprehensive indicators are used for evaluation of water contamination degree which makes possible to evaluate the contamination of water on a wide range of quality indicators at the same time. The values of these parameters are harmful for human health if they occurred more than defined limits. Developing methods for assessing water quality is an important issue. Therefore, the suitability of water sources for human consumption has been described in terms of Water quality index (WQI), which is one of the most effective ways to describe the quality of water. Development and implementation of indexation methods used in the assessment of surface water quality (pollution) is particularly relevant in recent years<sup>2,7-17</sup>. Currently, hydrological practice actively uses several dozen indices. It must be noted that most developing complex characteristics of water object in one way or another is connected with the existing maximum permissible concentration (MPC) (Refs 2, 18 and 19). As a result of anthropogenic pollution of aqueous environment properties are changed, the isolated compounds are oxidised and entropy of system is changed, which are not always taken into account in hydrochemical studies. Recently was suggested entropic water quality index (EWQI) and Armenian water quality index (AWQI) for evaluation of surface water quality<sup>16,20-22</sup>. The evaluation of water quality in the rivers Akhurtan, Ashotsk and Karkachun by EWQI is the aim of the present paper.

## EXPERIMENTAL

### STUDY AREA

Akhuryan is a river running along the Armenian plateau in the South Caucasus. It is the left tributary of Arax. In the upper current flows through the territory of Armenia, in the lower one – along the border of Armenia with Turkey. It flows from the Arpilis reservoir, flows into the Araks near the village of Bagaran<sup>1</sup>. The river Akhuryan has length of 186 km and river basin of 9670 km<sup>2</sup>. There are 5 monitoring posts on the Akhuryan River: No 31 – 0.5 km above Amasia City; No 32 – 1.0 km below Amasia City; No 33 – 1.0 km above Gyumri City; No 34 – 5.0 km below Gyumri City; No 35 – 0.5 km below Ervandashat village<sup>19</sup>. The river Ashotsk has length of 20 km and river basin of 197 km<sup>2</sup>, it is the left tributary of the Akhuryan river. There are 2 monitoring posts, No 36 – 0.5 km below the Artashen village and No 37 – at the mouth of the river. The river Karkachun has length of 55 km and river basin of 1220 km<sup>2</sup>, it is the left tributary of the Akhuryan river. There is a monitoring post, No 38 – 0.5 km below the Garibjanyan village.

PROCEDURE FOR DETERMINING INDEXES

*Entropic water quality index (EWQI) and Armenian water quality index (AWQI)*. The concept of entropy has many interpretations in various fields of human knowledge. The system interacts with the outside world as a whole. An open system can exchange energy, material and, which is not less important, information with environment. The system consumes information from the environment and provides information to environment for act and interact with environment. Shannon<sup>24</sup> was the first who related concepts of entropy and information. He has suggested that entropy is the amount of information attributable to one basic message source, generating statistically independent reports. Get any amount of information entropy is equal to the lost. Information entropy for independent random event  $x$  with  $N$  possible states is calculated by the following equation:

$$H = - \sum_{i=1}^N P_i \log_2 P_i$$

where  $P_i$  is the probability of frequency of occurrence of an event.

Entropy general equation of Shannon was been used at the first by Maq-Artur for evaluation of degree of structuring biogenesis<sup>25</sup>. Margalef postulated theoretical concept that meets a variety of entropy for a random selection of species from the community<sup>26</sup>. As a result of these works widespread and universal recognition received index Shannon  $H$ , sometimes referred to as a Shannon information index of diversity<sup>24</sup>:

$$H = - \sum n_i / N \log_2 (n_i / N).$$

Different processes in hydroecological systems both with increasing and decreasing of entropy can occur. Pollution of water systems can be represented as a system of the hydro-chemical parameters (elements), the concentration of which exceeds the MPC. Then in the equation Shannon  $P_i$ - probability of the number of cases of MPC excess of  $i$ -substance or water indicator of total cases of MPC –  $N$ ,  $P_i = n_i / N$ .

The following computational algorithm is used for determination of EWQI and AWQI values:

1. Determines the number of cases of MPC excess of  $i$ -substance or indicator of water –  $n$ .
2. Estimates the total amount of cases the maximum permissible concentration (N) –  $N = \sum n$ .
3. Computes  $\log_2 N$ ,  $n \log_2 n$  and  $\sum n \log_2 n$ .
4. Determines geoeological syntropy<sup>27</sup> ( $I$ ) and entropy ( $H$ ):  
 $I = \sum n \log_2 (n/N)$  and  $H = \log_2 N - I$ .
5. Then EWQI is determined:  $EWQI = H/I$ .
6. Further, the total amount multiplicity of MAC exceedances is estimated ( $M$ ) –  $M = \sum m$ .
7. Computes  $\log_2 M$ .

8. Finally, Armenian water quality index was obtained:  $AWQI = EWQI + 0.1 \log_2 M$ .

Therefore, five categories have been suggested to categorise the water qualities which are summarised in Table 1.

**Table 1.** Classes of water quality depending on the value of EWQI and AWQI

EWQI value	AWQI value	Rating of water quality	Water quality classes
< 0.7	<1.1	excellent water quality	1
0.7–1.0	1.1–1.4	good water quality	2
1.0–1.4	1.4–1.8	fair water quality	3
1.4–1.7	1.8–2.1	marginal water quality	4
>1.7	> 2.1	poor water quality	5

*Water contamination index (WQI).* WQI is established by the USSR Goskomgidromet<sup>7</sup> and belongs to the category of indicators most often used to assess the quality of water bodies. This index is a typical additive coefficient and represents the average percentage of exceeding the MPC for a strictly limited number of individual ingredients:

$$WQI = \frac{1}{n} \sum_{i=1}^n \frac{C_i}{MPC_i}$$

where  $C_i$  is the concentration of the component (in some cases – the value of the physicochemical parameter);  $n$  – the number of indicators used to calculate the index,  $n = 6$  (pH, biological oxygen demand of BOD<sub>5</sub>, dissolved oxygen in water, BOD<sub>5</sub>, petroleum products, nitrite ions (NO<sub>2</sub><sup>-</sup>), and ammonium ion (NH<sub>4</sub><sup>+</sup>)); MPC<sub>*i*</sub> – the established value of the standard for the relevant type of water body. To calculate the water pollution index for the entire set of standardised components, including the pH-value, the biological oxygen demand of BOD<sub>5</sub> and the dissolved oxygen content, the  $C_i/MAC$  ratios of the actual concentrations are found to be the MPC and the obtained list is sorted. The WQI is calculated strictly according to six indicators having the highest values of the given concentrations, regardless of whether they exceed the MPC or not. When calculating the IZV for the components  $C_i/MAC_p$ , the following conditions apply unambiguously to the normed components:

- for biological oxygen consumption BOD<sub>5</sub> (maximum permissible concentration – 3 mg O<sub>2</sub>/dm<sup>3</sup> for water bodies for domestic and drinking water use and not more than 6 mg O<sub>2</sub>/dm<sup>3</sup> for water bodies for domestic and cultural water use), special values of standards are established, depending on the very value of BOD<sub>5</sub>:

BOD <sub>5</sub> (mgO <sub>2</sub> / dm <sup>3</sup> )	Value of the standard (MPC)
Less than 3	3
3 to 15	2
More than 15	1

• the concentration of dissolved oxygen is normalised to the exact opposite: its content in the sample should not be less than 4 mg/dm<sup>3</sup>, therefore for each range of concentrations of the component, special values of the terms  $C_i/MPC_i$  are set:

Concentration (mgO <sub>2</sub> /dm <sup>3</sup> )	Value of the term $C_i/MPC_i$
Greater than or equal to 6	6th
Less than 6 to 5	12
Less than 5 to 4	20
Less than 4 to 3	30
Less than 3 to 2	40
Less than 2 to 1	50
Less than 1	60

•For the value of pH, the current standards for water in reservoirs for various purposes regulate the range of permissible values in the range from 6.5 to 8.5, therefore, for any excess pH exceeding the limits of this range, special values of the  $C_i/MPC_i$ .

pH value is below the normal range (<6.5)	pH above normal range (> 8.5)	Value of the summand $C_i/MPC_i$
Less than 6.5 to 6	over 8.5 to 9	2
Less than 3 to 5	more than 9 to 9.5	5
Less than 5	more than 9.5	20

Depending on the magnitude of the IWW, water body sites are divided into classes (Table 2). It is required that water pollution indices be compared for water bodies of one biogeochemical province and of a similar type for the same watercourse (with the flow, in time, etc.) and also taking into account the actual water availability of the current year.

**Table 2.** Classes of water quality depending on the value of WCI

WCI value	Rating of water quality	Water quality classes
up to 0,2	very clean	I
0.2–1.0	clean	II
1.0–2.0	moderately polluted	III
2.0–4.0	contaminated	IV
4.0–6.0	dirty	V
6.0–10.0	very dirty	VI
> 10.0	extremely dirty	VII

*Canadian Council of Ministers of the Environment water quality index (CWQI).* CWQI provides a consistent method, which was formulated by Canadian jurisdictions to convey the water quality information for both management and the public.

Moreover, a committee established under the Canadian Council of Ministers of the Environment (CCME) has developed WQI, which can be applied by many water agencies in various countries with slight modification. This method has been developed to evaluate surface water for protection of aquatic life in accordance to specific guidelines. The parameters related with various measurements may vary from one station to the other and sampling protocol requires at least four parameters, sampled at least four times<sup>9</sup>. The calculation of index scores in CWQI method can be obtained by using the following relation:

$$CWQI = 100 - \frac{(F_1^2 + F_2^2 + F_3^2)^{1/2}}{1.732},$$

where scope ( $F_1$ ) is the number of variables, whose objectives are not met,  $F_1 = [\text{No of failed variables}/\text{total no of variables}] \times 100$ ; frequency ( $F_2$ ) – the number of times by which the objectives are not met,  $F_2 = [\text{No of failed tests}/\text{total no of tests}] \times 100$ ; amplitude ( $F_3$ ) – the amount by which the objectives are not met.

(a) The number of times by which an individual concentration is greater than (or less than, when the objective is a minimum) the objective is termed an ‘excursion’ and is expressed as follows (when the test value must not exceed the objective):

$$\text{excursions}_i = [\text{Failed test value}_i/\text{objective}_i] - 1;$$

(b) The collective amount by which individual tests are out of compliance is calculated by summing the excursions of individual tests from their objectives and dividing by the total number of tests (both those meeting objectives and those not meeting objectives). This variable, referred to as the normalised sum of excursions, or nse, is calculated as:

$$\text{normalised sum of excursions (nse)} = \sum_{i=1}^n \text{excursions}_i / \text{No of tests}$$

$$(c) F_3 = [\text{nse}/0.01\text{nse} + 0.01]$$

Therefore, five categories have been suggested to categorise the water qualities which are summarised in Table 3.

**Table 3.** Classes of water quality depending on the value of CWQI

CWQI value	Rating of water quality	Water quality classes
95–100	excellent water quality	1
80–94	good water quality	2
60–79	fair water quality	3
45–59	marginal water quality	4
0–44	poor water quality	5

*Specific combinatory water quality index (SWQI).* In accordance with RD 52.24.643-2002, ‘The method for the integrated assessment of the degree of contamination of surface waters by hydrochemical indicators’ ‘ws introduced the calculation of the

specific combinatorial water quality index<sup>8</sup>. To assess the quality of water in rivers and water bodies, they are divided by contamination into several classes. The classes are based on the intervals of the specific combinatory water pollution index, depending on the number of critical pollution indicators. At least 15 indicators are analysed. Required list includes: dissolved oxygen in water, BOD<sub>5</sub>, chemical oxygen consumption – COD, phenols, petroleum products, nitrite ions (NO<sub>2</sub><sup>-</sup>), nitrate ions (NO<sub>3</sub><sup>-</sup>) ammonium ion (NH<sub>4</sub><sup>+</sup>), iron total (Fe<sup>2+</sup> and Fe<sup>3+</sup>), copper (Cu<sup>2+</sup>), zinc (Zn<sup>2+</sup>), nickel (Ni<sup>2+</sup>), manganese (Mn<sup>2+</sup>), and chlorides and sulphates.

**Table 4.** Surface water quality categories

Class and rank	Characteristics of the state of water pollution	Specific combinatorial index of water pollution					
		without regard to the number of bullpen	depending on the number of accountable bullpen				
			1	2	3	4	5
1st	conditionally pure	1	0.9	0.8	0.7	0.6	0.5
2nd	slightly contaminated	12	0.9–1.8	0.8–1.6	0.7–1.4	0.6–1.2	0.5–1.0
3rd	contaminated	2–4	1.8–3.6	1.6–3.2	1.4–2.8	1.2–2.4	1.0–2.0
Discharge ‘a’	contaminated	2–3	1.8–2.7	1.6–2.4	1.4–2.1	1.2–1.8	1.0–1.5
Rank ‘b’	very polluted	3–4	2.7–3.6	2.4–3.2	2.1–2.8	1.8–2.4	1.5–2.0
4th	dirty	4–11	3.6–9.9	3.2–8.8	2.8–7.7	2.4–6.6	2.0–5.5
Discharge ‘a’	dirty	4–6	3.6–5.4	3.2–4.8	2.8–4.2	2.4–3.6	2.0–3.0
Rank ‘b’	dirty	6–8	5.4–7.2	4.8–6.4	4.2–5.6	3.6–4.8	3.0–4.0
Rank ‘B’	very dirty	8–10	7.2–9.0	6.4–8.0	5.6–7.0	4.8–6.0	4.0–5.0
Grade ‘g’	very dirty	8–11	9.0–9.9	8.0–8.8	7.0–7.7	6.0–6.6	5.0–5.5
5th	extremely dirty	11 and more	9.9 and more	8.8 and more	7.7 and more	6.6 and more	5.5 and more

The value of SWQI is determined by the frequency and the multiplicity of the MPC exceeding by several indicators and can vary in waters of different degree of contamination from 1 to 16 (for pure water 0). The higher the index value corresponds to the worst water quality. Taking into account the number of bullpen, allows you to divide the surface waters into 5 classes, depending on the degree of their contamination. The 3rd and 4th classes for a more detailed water quality assessment are divided into 2 and 4 categories, respectively. The classification of water quality is given in Table 4.

## RESULTS AND DISCUSSION

### RIVER AKHURYAN

It was established in the river Akhuryan water is regularly increased MPC of copper, vanadium, aluminum, chrom, manganese and iron<sup>23</sup>. For example, in position No 34 of river Akhuryan NO<sub>2</sub><sup>-</sup>, NH<sub>4</sub><sup>+</sup>, Al, V, Cu, Mn, Fe and Cr number of MPC increas-

ing cases are 6, 6, 7, 7, 7, 6, 4 and 5 times, respectively. The amount of excess cases of MPC –  $N = 46$ ,  $\sum n \log_2 n = 105.38$ ,  $I = 105.38/48 = 2.195$ ,  $H = \log_2 48 - 2.195 = 5.581 - 2.195 = 3.386$ ,  $EWQI = G = 3.386/2.195 = 1.5423$ . The total amount of the multiplicity of MPC exceedances –  $M = \sum m = 42$ ,  $\log_2 M = 5.389$ ,  $AWQI = 1.5423 + 0.5389 = 2.081$  (Table 5).

**Table 5.** Entropic and Armenian water quality indexes for the Akhurtan river

Positions	31		32		33		34		35	
Indicator	$n$	$n \log_2 n$	$n$	$n \log_2 n$	$n$	$n \log_2 n$	$n$	$n \log_2 n$	$n$	$n \log_2 n$
$\text{NO}_2^-$	0	0	0	0	0	0	6	15.5	0	0
$\text{NH}_4^+$	0	0	0	0	0	0	6	15.5	0	0
Al	6	15.5	7	19.64	7	19.64	7	19.64	5	11.6
V	6	15.5	7	19.64	7	19.64	7	19.64	7	19.64
Cu	4	8	4	8	6	15.5	7	19.64	4	8
Mn	0	0	4	8	6	15.5	6	15.5	4	8
Fe	0	0	0	0	3	4.75	4	8	0	0
Cr	0	0	0	0	0	0	5	11.6	2	2
N	16		22		29		48		22	
$\sum n \log_2 n$	39		55.28		75.03		105.38		49.24	
$I$	2.4375		2.512		2.59		2.1954		2.238	
$H$	1.5625		1.945		2.265		3.386		2.219	
EWQI	0.641		0.774		0.8745		1.5423		0.991	
$M = \sum m$	17.8		20.4		32.6		42		17.8	
$\log_2 M$	4.151		4.348		5.024		5.389		4.151	
AWQI	1.056		1.2088		1.3469		2.081		1.4065	

It was shown that from the source to the mouth of the river there is an increase in the value of the EWQI, which indicates the decline in the quality of water of the rivers from the first to the fourth class of pollution. After the cities of Amasia and Gyumri AWQI increases, indicating a decrease in water quality due to pollution of water in the River Akhuryan by domestic wastewaters.

#### RIVERS ASHOTSK AND KARKACHUN

It was established in the river Ashotsk water is regularly increased MPC of copper, vanadium, aluminum. It has been shown that from the source to the river mouth there is an increase in the cost of AWQI, however, water quality remains of the first class (Table 2).

For the river Karkachun water quality of the second class. For example, in the position No 38 of river Karkachun  $\text{NO}_2^-$ ,  $\text{NH}_4^+$ , Al, V, Cu and Mn number of MPC increasing cases is 7, 5, 5, 7, 6, and 6 times, respectively (Table 6).



**Table 6.** Entropic and Armenian water quality indexes for the Ashotsk and Karkachun rivers

River Positions Indicator	Ashotsk				Karkachun	
	36		37		38	
	<i>n</i>	<i>n log<sub>2</sub>n</i>	<i>n</i>	<i>n log<sub>2</sub>n</i>	<i>n</i>	<i>n log<sub>2</sub>n</i>
NO <sub>2</sub> <sup>-</sup>	0	0	0	0	7	19.64
NH <sub>4</sub> <sup>+</sup>	0	0	0	0	5	11.6
Al	4	8	6	15.5	5	11.6
V	1	0	6	15.5	7	19.64
Cu	0	0	4	8	6	15.5
Mn	0	0	0	0	6	15.5
<i>N</i>	5		16		36	
$\sum n \log_2 n$	8		39		93.48	
<i>I</i>	1.6		2.4375		2.59	
<i>H</i>	0.72		1.5625		2.576	
EWQI	0.45		0.641		0.995	
M= $\sum m$	4.1		15.1		29.8	
log <sub>2</sub> M	2.03		3.914		4.894	
AWQI	0.653		1.032		1.4844	

The quality of rivers Akhurtan, Ashotsk and Karkachun water also comprehensively evaluated by other indexes: WCI, EWQI, CWQI, SCWQI (Table 7).

**Table 7.** WQI for the Akhurtan, Ashotsk and Karkachun rivers

Index	AWQI	EWQI	WQI	CWQI	SCWQI
31	1.0561	0.6410	1.78	71.58	1.77
32	1.2088	0.7740	1.81	68.37	1.96
33	1.3469	0.8745	2.65	63.04	2.01
34	2.0810	1.5423	4.87	57.04	2.64
35	1.4065	0.9910	2.09	71.40	2.17
36	0.6530	0.4500	0.64	92.20	0.92
37	1.0320	0.6410	1.63	68.51	1.44
38	1.4844	0.9950	4.00	58.99	2.15

With the help of the computer program ‘Origin-6’ is done an analysis of the linear relationship between EWQI and other WQI:  $EWQI = a + b(WQI)$ . A good correlation is obtained also when the rivers Akhurtan, Ashotsk and Karkachun are considered together:

$$EWQI = (0.334 \pm 0.146) + (0.219 \pm 0.050)WCI; R = 0.89103; N = 7;$$

$$EWQI = -(0.659 \pm 0.267) + (0.783 \pm 0.130)SCWQI; R = 0.93702; N = 7;$$

$$EWQI = -(0.271 \pm 0.040) + (869 \pm 0.029)AWQI; R = 0.99732; N = 7;$$

$$EWQI = (3.488 \pm 1.032) - (0.039 \pm 0.016)CWQI; R = 0.74469; N = 7.$$

Thus, a correlation between EWQI and other WQI is established. Analysis of obtained data indicates that EWQI has liner dependence on WCI, SCWQI, AWQI and an inverse dependence on CWQI.

## CONCLUSIONS

1. It was established in the river Akhuryan water is regularly increased MPC of copper, vanadium, aluminum, chrom, manganese and iron. It was shown that from the source to the mouth of the river there is an increase in the value of the EWQI and AWQI, which indicates the decline in the quality of water of the rivers from the 1st to the 4th class of pollution. The CWQI and SPWQI are reduced from the 2nd to the 3rd pollution class, and the WCI is reduced from the 3rd to the 5th contamination class. After the cities of Amasia and Gyumri WQI increases, indicating a decrease in water quality due to pollution of water in the river Akhuryan by domestic. wastewaters.

2. It has been shown for river Ashotsk that from the source to the river mouth there is an increase in the cost of entropic water quality index, however, water quality remains of the first class, and for the river Karkachun water quality of the second class.

3. With the help of the computer program 'Origin-6' is done an analysis of the linear relationship between EWQI and other WQI. Analysis of obtained data indicates that EWQI has inverse dependence on CWQI and liner dependence on WCI, SCWQI, AWQI.

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