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ASSESSING THE CHEMICAL STATE OF THE DEBED RIVER GIVEN THE NATURAL BACKGROUND CONCENTRATIONS OF THE HYDROCHEMICAL PARAMETERS

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Natural background concentrations have been used to assess the chemical status of the Debed River basin. Natural background concentrations (BGC) of hydrochemical parameters are calculated by the function of theoretical logarithmic distribution. A site-specific classification system for the assessment of the water quality of the Debed River basin based on BGC is developed. The water quality of the Debed River from the town of Spitak to the city of Vanadzor is ranked as a "moderate" quality, after Vanadzor -"bad" and after the mixing of the rivers Dzoraget and Marts to the Armenian-Georgian border -"good". The main pollutants in the basin are revealed and their impact is assessed.

Keywords: background concentration, chemical quality, water quality classification.

Introduction. Armenia’s current system of surface water quality assessment is based on the maximum permissible concentrations (MPC) for fisheries inherited from the former Soviet Union [1]. The main disadvantage of MPC is that the terrain peculiarities and natural background content of parameters are not taken into account. Besides, these norms are designed for large river systems and the water resource was estimated only for the purposes of fisheries and protection of aquatic life. MACs for some parameters, such as copper, vanadium, chromium, are unreasonably very low and for the nutrients, such as nitrate and phosphate, on the contrary- very high.

According to the European Union 78/659/EEC directive for fisheries, for total zinc, "I" values are, respectively, 30 (salmonid) and 100 (cyprinid) times higher than the MAC applied in Armenia. MAC for copper applied in Armenia (0.001 *mg/l*) is 40 times higher than EU Guide value (0.04 *mg/l*). Furthermore, in the source of the Pambak River which does not carry the anthropogenic impact copper concentration is 2…3 times higher than the MPC. From this perspective, using the MAC characteristic, the pollutants of the river basin and the real impacts on the water quality is not possible to determine.

MACs, due to the existing shortcomings, are not an appropriate way to assess the surface water pollution. There is a need to develop new standards and an assessment system that would enable to discover the true pressures on the water quality and their degree.

For this purpose, the international experience of assessing the water quality has been investigated [2-9]. Taking into account the fact that there are only physical-chemical water quality monitoring data for the Debed river basin, it is decided to develop an evaluation system based on physico-chemical indicators of water quality.

The goal of the present study is to develop a new system for the assessment of water quality of the Debed River basin based on the natural background concentrations of hydrochemical parameters.

There are different methods to define the background concentrations of chemical and physico-chemical elements in literature. For example, mean value plus two standard deviations, 90th percentile value, the median value, geochemical, statistical, combined methods [10].

In the presented work, BGCs are calculated using the statistical method with the theoretical distribution function, which takes into account the correlation coefficient based on geochemical expert judgment [8, 9]. This method is quite simple, and for calculation, long-term water quality data are not required.

Methodology of Calculation Site-Specific Background Concentrations. Since, in the nature the processes are mainly described as a normal distribution function, and in mathematical statistics variables rank, regardless of their distribution law, seeking to normality, it is accepted that the theoretical distribution function considers the probability density function of the lognormal distribution.

The probability density function of the lognormal distribution with parameters μ and σ is given as follows:

$$f(x) = \frac{1}{x\sigma\sqrt{2\pi}} exp\left(-\frac{1}{2}\frac{(ln(x)-\mu)^2}{\sigma^2}\right), \; x > 0,$$

where μ and σ are the location and scale parameters respectively, which can be estimated as follows:

$$\hat{\mu} = \frac{\sum_{i=1}^{n} ln(x_i)}{n}, \qquad \hat{\sigma}^2 = \frac{\sum_{i=1}^{n}(ln(x_i)-\mu)^2}{n}.$$

The lognormal distribution function percentile is calculated as follows:

$$x_p = F^{-1}\left(\frac{p}{100}\right),$$

where F(x) is the lognormal cumulative distribution function.

If the theoretical logarithmic function is used instead of the empirical distribution function, F(x) is estimated as follows:

$$F(x) = \frac{\# X \leq x}{n+1},$$

where $\#X \leq x$ shows number of observations that are smaller than or equal to x:

Percentiles for the empirical data are calculated as follows:

$$x_p = x_{[k]} + (d * (x_{[k+1]} - x_{[k]})), \quad 0 < k < n$$

$$x_p = \begin{cases} x_1, k = 0 \\ x_n, k = n \end{cases}$$

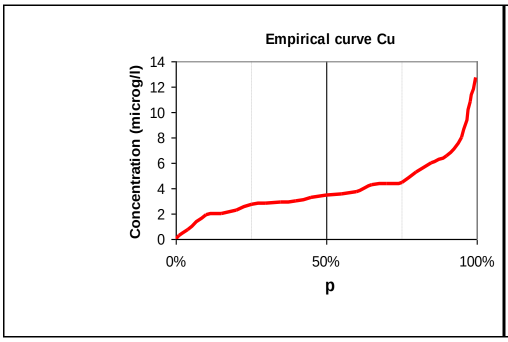
$$R = 1 + \left(\frac{p}{100} * (n-1)\right), \; R = k + d,$$

x_p is the value of p^{th} percentile in the database, $x_{[k]}$ is the number of k^{th} in the database sorted in ascending order, p is the integer from 0 to 100 (percentile percentage value), n is the total number of observations, R is a place of p percentile in database sorted in ascending order, k is the whole part of R, d is the fractional part of R.

Results and discussion. First of all, for assessing background concentrations of hydrochemical parameters for the Debed River basin, the location with natural or minimal anthropogenic influence, where water quality data are available, should be chosen. From the existing monitoring sites in the Debed River basin the Pambak-source has been selected. Pambak is the tributary of the Debed River.

For calculating the BGCs, water monitoring data for the period 2006-2010 were used [11]. The sequence of steps in the implementation of the BGCs calculations is presented below:

- the hydrochemical monitoring data are aggregated,
- the μ and σ parameters are calculated;
- the percentile is calculated in the range of 50-90%;
- the logarithmic normal distribution curve then the trend are built;
- the BGCs values are estimated from the lognormal probability curve as percentile, where sudden concentrations arise appeared (Fig.).



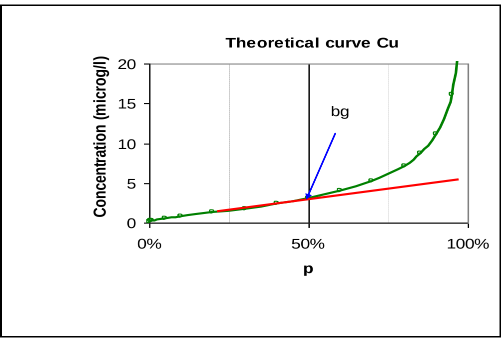


Fig. Empirical and theoretical curves for the BGC determination

BGCs calculations were carried out with both theoretical and empirical distribution functions. 70…80% of the estimated result values obtained from theoretical and empirical distribution curves are the same. For the remaining 20…30% of the cases, as a final result, the values derived from the theoretical distribution curve taking into account the limitations of our data are mainly taken, because in this case, the value derived from the theoretical distribution curve can be considered more reliable.

For the simplification of calculations of BGCs, a special computer program has been developed.

Comparing the BGCs in urban and non-urban areas in the Debed River basin. The composition and concentration of substances in surface water is a resultant of two factors: the geological structure of the earth's crust including the intensity with which it is leached, and the anthropogenic activity associated with agriculture, industry and public utilities. Thus, BGCs of substances in different parts of the river can vary significantly. BGCs of sampling sites with minimal anthropogenic impact may differ essentially and lead to an incorrect assessment of the water quality. The increase of concentration of any hydrochemical parameter is possible which is typical of a location.

To understand the variation of the contents of water quality parameters across the Debed River, BGCs for all sampling sites of the river have been calculated (Table 1). As an urban area, the sampling sites 0.5 *km* before (Water quality monitoring site N3) and 0.5 *km* after (Water quality monitoring site N4) the city of Vanadzor were taken. As a non-urban area the sampling site located on the mouth of the Marts river (Water quality monitoring site N13), which is the tributary of the Debed river, was taken. The main anthropogenic impacts on the Marts are agriculture and non-point pollution of domestic sewage. Sampling site N7 is the last site on the Armenian-Georgian border and Sampling site N5 is the first point of the Debed River after mixing with Pambak, Dzoraget, and Marts rivers [10].

The obtained results have shown that in general, the water quality parameters according to the variation of BGCs can be divided into the following groups:

Group I includes ammonium, nitrite, nitrate and phosphate ions, total phosphorus. Concentrations of this group have increased sharply after settlements especially after the city of Vanadzor due to the flow of urban domestic wastewater into the river without treatment.

Group II includes sulfate and chloride ions, TDS, sodium, magnesium, potassium, calcium, titanium, vanadium, chromium, manganese, nickel, molybdenum, stibiume, boron and lithium, whose concentrations increase in the upper stream of the river (sodium, boron, and lithium in 3…4 times, and the remaining parameters 1.2…2.0 times) while in subsequent sites after Vanadzor they remain almost unchanged, and even decrease after mixing of Dzoraget and Marts. Therefore, the content of this group is caused by the geohydrochemical nature of the region.

Group III includes copper, zinc, lead, and suspended solids whose content increases after Vanadzor, but more significantly after Enrichment plant of Akhtala (sampling site N 7). Cadmium and barium contents increase 1.2…1.4 times, the remaining sampling sites are unchanged.

The comparison of rural (sampling site N 13) and without anthropogenic impact (sampling site N 1) sites shows that sodium, magnesium, boron, lithium, aluminum, potassium, magnesium, copper, zinc, arsenic, barium, selenium, cadmium, chromium, cobalt, and manganese content is 1.2…3.0 times higher in Martz. Other parameters' content is almost the same in both sites.

Table 1

BGCs for the water quality monitoring sites of the Debed River Basin

Water quality parameters	Sampling sites					
	1 (BGC)	**3**	**4**	**5**	**7**	**13**
Ammonia ion, *mgN/l*	0.19	0.25	1.35	0.31	0.22	0.18
Nitrite ion, *mgN/l*	0.012	0.032	0.070	0.047	0.036	0.011
Nitrate ion, *mgN/l*	1.62	3.43	4.32	2.02	2.17	1.65
Phosphate ion, *mg/l*	0.031	0.035	0.098	0.068	0.075	0.030
Sulfate ion, *mg/l*	35.4	43.2	50.5	29.8	44.2	30.7
Chloride ion, *mg/l*	6.3	9.0	11.8	9.0	7.8	5.7
Suspended solids, *mg/l*	2.8	22.9	32.5	20.6	51.2	14.1
Total dissolved solids, *mg/l*	142.0	374.7	337.9	247.9	259.7	225.7
Li, *μg/l*	0.51	1.71	1.74	1.82	1.90	0.83
B, *μg/l*	16.8	61.0	67.0	61.0	43.0	21.9
Na, *mg/l*	9.0	24.1	26.1	24.1	16.0	12.3
Mg, *mg/l*	7.2	13.2	11.5	13.2	8.9	11.0
Al, *mg/l*	0.26	0.19	0.29	0.24	0.34	0.36
Total phosphorus, *mg/l*	0.05	0.09	0.22	0.10	0.11	0.06
K, *mg/l*	1.4	2.1	2.5	2.2	2.2	2.1
Ca, *mg/l*	40.0	52.0	55.0	37.5	35.9	43.9
Ti, *μg/l*	8.1	11.0	11.0	8.0	9.0	7.2
V, *μg/l*	2.9	4.1	3.6	4.9	4.0	2.6
Cr, *μg/l*	1.3	2.0	2.0	2.3	2.1	1.1
Fe, *mg/l*	0.09	0.45	0.45	0.25	0.56	0.24
Mn, *μg/l*	32.0	45.0	37.0	23.0	48.0	22.8
Co, *μg/l*	1.4	0.6	0.6	0.4	0.7	0.5
Ni, μg/l	1.1	1.7	1.6	1.4	1.7	1.3
Cu, *μg/l*	3.0	5.0	11.0	5.0	18.0	4.2
Zn, *μg/l*	4.3	7.0	11.0	6.0	19.1	5.7
As, *μg/l*	0.42	0.41	0.93	0.84	0.99	0.51
Se, *μg/l*	1.00	0.95	0.95	0.19	0.54	0.59
Mo, *μg/l*	0.76	1.04	1.45	1.02	1.04	0.68
Cd, *μg/l*	0.24	0.22	0.27	0.16	0.37	0.14
Sb, *μg/l*	0.22	0.30	0.39	0.19	0.49	0.22
Ba, *μg/l*	35.0	28.0	36.0	25.0	41.0	48.7
Pb, *μg/l*	0.66	1.25	2.06	1.16	2.84	0.75

Site-specific water quality assessment system. The development of site-specific water quality assessment system is a complicated process. Derivation of such a system requires extensive knowledge of the physical, chemical and biological characteristics of the water body under consideration, as well as the social and economic characteristics of the local area. This requires reliable and extensive biological monitoring data that does not yet exist in Armenia. An alternative method of setting objectives is the application of physico-chemical parameters. In this study, for the Debed River Basin site-specific water quality assessment, a system has been developed with application of calculated BGCs. The evaluation system has been developed taking into account the European Union's Water Framework Directive (WFD) approaches. According to the WFD, water quality is classified in class 5 (Table 2). These classes have color coding and they are used for mapping. The classification scheme is given in Table 3.

Table 2

Water quality classification

Class	Water quality	Color code
I	High	Blue
II	Good	Green
III	Moderate	Yellow
IV	Poor	Orange
V	Bad	Red

This water quality classification system is based on the idea “one out all out”. It means that if any parameter is classified "bad", then the water quality is "bad".

The substance concentrations corresponding to quality of class I characterize a condition free from anthropogenic impairments. The most stringent water quality target for the protected asset aquatic communities and fishing is defined by the quality class II, which therefore constitutes the aspired good water quality. Water body corresponding to subsequent classes 3-4 (quality classes moderate and poor) can be used for irrigation, industry, and hydropower.

The first quality class for the most parameters, besides dissolved oxygen, odor, color, BOD, COD, pH, is taken background concentrations.

The water quality in the Debed River 2012-2013. The water quality of the Debed River has been estimated for the period of 2012-2013. The evaluation has been done using the average annual concentrations. The results are shown in Table 4. Parameters which have been ranked as moderate, poor and bad classes are separated. At the same time, the water quality was assessed using the MAC, and parameters whose concentrations excess MPC are separated (Table 4).

The evaluation results indicate that the water quality of the Pambak-Debed River is deteriorating after mixing of untreated sewage of the Vanadzor and Spitak cities.

Later after mixing the Dzoraget and Marts Rivers, the water quality has improved again. The main pollutants of the river are nitrate, nitrite, ammonium and phosphate ions whose content's growth in the river is related to sewage and agricultural influence.

Table 3

Ecological State Classification in the Debed River Basin

Water quality parameters	Water quality class				
	I	II	III	IV	V
Ammonia ion, *mgN/l*	0.191	0.4	1.2	2.4	>2.4
Nitrite ion, *mgN/l*	0.012	0.06	0.12	0.3	>0.3
Nitrate ion, *mgN/l*	1.62	2.5	5.6	11.3	>11.3
Phosphate ion, *mg/l*	0.031	0.1	0.2	0.4	>0.4
Sulfate ion, *mg/l*	35.42	70.84	150	250	> 250
Chloride ion, *mg/l*	6.3	12.6	150	200	> 200
Suspended solids, *mg/l*	2.84	3.41	5.68	11.36	>11.36
Total dissolved solids, *mg/l*	142	284	1000	1500	>1500
B, *μg/l*	16.8	450	700	1000	2000
Na, *mg/l*	9.02	18.04	36.08	72.16	>72.16
Mg, *mg/l*	7.2	50	100	200	>200
Al, mg/l	0.26	0.52	1.03	5.00	>5.00
Total phosphorus, *mg/l*	0.05	0.2	0.4	1	>1
K, *mg/l*	1.4	2.8	5.6	11.2	>11.2
Ca, *mg/l*	40	100	200	300	>300
V, *μg/l*	2.9	5.8	11.6	23.2	>23.2
Cr, *μg/l*	1.3	11.3	100	250	>250
Fe, *mg/l*	0.09	0.18	0.5	1	>1.00
Mn, *μg /l*	32.0	64.0	128.0	256.0	>256.0
Co, *μg/l*	1.4	2.8	5.6	11.2	>11.2
Ni, *μg/l*	1.10	11.10	50	100	>100
Cu, *μg/l*	3.0	23.0	50	100	>100
Zn, *μg/l*	4.3	100	200	500	>500
As, *μg/l*	0.42	20	50	100	>100
Se, *μg/l*	1.0	20.0	40.0	80	>80
Mo, *μg/l*	0.76	1.52	3.04	6.08	>6.08
Cd, *μg/l*	0.24	1.24	2.24	4.24	>4.24
Sb, *μg/l*	0.22	0.44	0.88	1.76	>1.76
Ba, *μg/l*	35.0	70.0	140.0	1000	>1000
Pb, *μg/l*	0.66	10.66	25	50	>50
Dissolved oxygen, mgO_2/l	>7	>6	>5	>4	<4
BOD_5, mgO_2/l	3	5	9	18	>18
COD-Cr, *mgO/l*	10	25	40	80	>80
Odor, *degree*	natural	2	2	4	>4
Color, *degree*	natural	<5	20	30	>200
pH	natural	6.5-9.0			

The comparison with MPC has shown that in the first site without anthropogenic influence, concentration of B, Al, V, Cu and Mn parameters exceeds the corresponding MPCs. The list of detected pollutants using MPC's is substantially different from the list obtained from the classification based on BGCs and does not reflect the actual pollution sources and types of pollutants.

Table 4

Water quality in the Debed River at the sampling sites 1-7

S.S	Water quality class	According to this parameter	Parameters exceeding MPC
I	High (I class)	-	B, Al, V, Cu, Mn
2	Moderate (III class)	Nitrate ion	Nitrite ion, B, Al, V, Cu, Mn, Cr
3	Moderate (III class)	Nitrite ion, Nitrate ion, SS	Nitrite ion, B, Al, V, Cu, Mn, Cr, SS
4	Moderate (III class) Bad (V class)	Nitrite ion, Nitrate ion, SS, TP Ammonia ion, Phosphate ion	Nitrite ion, Ammonia ion, SS, BOD_5, B, Al, V, Cu, Mn, Cr
5	Good (II class)	-	Nitrite ion, B, Al, V, Cu, Mn, Cr
6	Good (II class)	-	Nitrite ion, B, Al, V, Cu, Mn, Cr, Zn, Se
7	Good (II class)	-	Nitrite ion, B, Al, V, Cu, Mn, Cr, Zn

Conclusion. Logarithmic normal distribution function is an effective tool for the assessment of background concentrations. Application of background concentrations on the assessment of the river water quality has made it possible to estimate the pollution and the real impact on the water quality.

The list of detected pollutants using MPC's is substantially different from the list obtained from the classification based on BGCs and does not reflect the actual pollution sources and types of pollutants.

The water quality of the Debed River deteriorates after mixing of sewage (point and non-point pollution) from the large community. The main pollutants of the river are nitrate, nitrite, ammonium and phosphate ions.

The water quality of the Debed River after the city of Spitak to Vanadzor is ranked in "moderate" class, after Vanadzor-"bad", after the mixing of the rivers Dzoraget and Marts rivers on the Armenian-Georgian border -"good".

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ԴԵԲԵԴ ԳԵՏԻ ՔԻՄԻԱԿԱՆ ԿԱՐԳԱՎԻՃԱԿԻ ԳՆԱՀԱՏՈՒՄԸ ՋՐԱՔԻՄԻԱԿԱՆ ՑՈՒՑԱՆԻՇՆԵՐԻ ԲՆԱԿԱՆ ՖՈՆԱՅԻՆ ԿՈՆՑԵՆՏՐԱՑԻԱՆԵՐԻ ԿԻՐԱՌՄԱՄԲ

Գ.Ա. Շահնազարյան

Դեբեդ գետի ավազանի քիմիական կարգավիճակի գնահատման համար կիրառվել է «բնական ֆոնային կոնցենտրացիայի» մոտեցումը: Ջրաքիմիական ցուցանիշների բնական ֆոնային կոնցենտրացիան (ԲՖԿ) հաշվարկվել է տեսական լոգարիթմական բաշխման ֆունկցիայի միջոցով: Մշակվել է Դեբեգ գետի ավազանի ջրերի որակի տեղանքին բնորոշ գնահատման համակարգը՝ հիմնված ԲՖԿ վրա: Դեբեդ գետի ջրի որակը Սպիտակ քաղաքից հետո մինչև Վանաձոր քաղաքը դասակարգվել է որպես «միջակ» որակ, Վանաձոր քաղաքից հետո՝ «վատ», իսկ Ձորագետ և Մարց գետերի խառնվելուց հետո, մինչև հայ-վրացական սահմանը՝ «լավ»: Բացահայտվել են ավազանի հիմնական աղտոտիչները, և գնահատվել է դրանց ազդեցության չափը:

Առանցքային բառեր. բնական ֆոնային կոնցենտրացիա, քիմիական որակ, ջրի որակի դասակարգում:

ОЦЕНКА ХИМИЧЕСКОГО СОСТОЯНИЯ РЕКИ ДЕБЕД С УЧЕТОМ ПРИРОДНЫХ ФОНОВЫХ КОНЦЕНТРАЦИЙ ГИДРОХИМИЧЕСКИХ КОМПОНЕНТОВ

Г.А. Шахназарян

Для оценки химического состояния бассейна реки Дебед использован подход природной фоновой концентрации (ПФК). ПФК гидрохимических показателей рассчитывались методом теоретической логарифмической распределительной функции. Разработан сайт - специфическая классификационная система для оценки качества воды реки Дебед, которая основана на ПФК. Качество воды реки Дебед после города Спитак до города Ванадзор оценилось по классу умеренно, после Ванадзора – плохо, после смешивания рек Дзорагета и Марца до армяно-грузинской границы - хорошо. Выявлены основные загрязнители бассейна и дана оценка степени воздействия.

Ключевые слова: природная фоновая концентрация, химическое качество, классификация качества воды.