

WATER SUPPLY, SEWERAGE, BUILDING CONSTRUCTION OF WATER RESOURCES PROTECTION

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E. G. Davydova¹

ANALYSIS OF THE QUALITY OF NATURAL WATER OF A RESERVOIR NEAR AN ORE EXTRACTION PLANT USING THE METHOD OF COMPLEX ASSESSMENT OF NATURAL WATER POLLUTION

Voronezh State Technical University

Russia, Voronezh, tel.: (473) 271-76-17, e-mail: davkat@mail.ru

¹PhD in Chemistry, Assoc. Prof. of the Dept. of Chemistry and Chemical Technology of Materials

Statement of the problem. At present close attention is paid to environmental safety of any new manufacturing, because the anthropogenic influence on the state of the river basin should be minimal. The solution to this problem is impossible without a complex assessment of the state of natural waters in a given area before and after the start of the activities of an ore mining plant on a number of hydrochemical indicators.

Results. Complex hydrochemical indices of contamination of samples taken in the zone of impact of ore mining are determined. An excess of the maximum permissible concentrations for the content of iron, copper, zinc, manganese, chemical and biological oxygen consumption was found. According to the obtained values of the specific combinatorial water quality Index, it is established that the water being studied is characterized as very polluted. By the multiplicity of exceeding the MPC, the level of contamination is characterized as high.

Conclusions. It has been established that in the period of an increased runoff, stable pollutants are zinc, iron and copper. It is assumed that the technogenic factor plays an important role in increasing the concentration of these elements. The results allows one to predict the effect of possible impacts of mining sulfide copper-nickel deposits on aquatic ecosystems of vast adjoining territories in the Novokhopersky region.

Keywords: hydrochemical indicators of contamination, maximum permissible concentrations, specific combinatorial water quality Index, natural water.

Introduction. It is known that 2012 the Ural Mining and Metallurgical Company (UMMC) won the first prize at a contest of sulfide copper-nickel mines in Novokhoperskiy district of Voronezh region where geological mining is now taking place [12]. In mass media there has

been a heated debate between those supporting and opposing the nickel project. Therefore it is necessary to analyze possible outcomes of a mining production in Voronezh region in terms of its effect on the chemical composition of surface water.

According to [16], a mining complex is the largest source of industrial waste contributing to an exponential growth of environment pollution. Presently most wastes are associated with the Ural Federal District, district of the Kursk Magnetic Anomaly, Tula and Ryazan regions. Over 500 thousand hectares of land in Russia are taken up by mining industrial storages and the area that is 10—15 times of that is impacted by environmental waste with about 80 billion tons of solid waste only are accumulated in dumps and other storages across the country. Around 10 thousand hectares employed for dumps is suitable for agriculture [4]. If nickel starts being mined in Voronezh region, our region will be facing these issues as well.

The importance of the study is due to the danger posed by this type of mining that leads to the pollution of surface water ecosystems by industrial waste. The major source of technological substances coming into water flows is discharge from mines, mining plants, storages as well as dumps. Acid discharge waters are particularly dangerous as they contain a lot of metals that are mobile and in high concentrations that are considerably over the maximum permissible concentration (MPC) [3].

Apart from poisonous substances, non-organic impurities that are emitted in nickel and zinc industries, oxidative processes are also hazardous and result from the oxygen reduction in water and an increase in its biochemical consumption, which leads to the degradation of the organoleptic indices of water. Such metals as mercury, cadmium, lead, chrome, copper, nickel are accumulated in water reservoirs and have an impact on bacteria that mineralize active substances [6].

The existing methods of comprehensive evaluation of the pollution of surface water are grouped as follows: the first group are the methods that evaluate the quality of water according to a set of hydrochemical, hydrophysical, hydrobiological, microbiological indices; the second group are the methods that involve calculations of complex indices of water pollution.

The use of complex indices allows to address the following:

- 1) a quantitative evaluation of water pollution simultaneously along a wide range of ingredients and quality indices;
- 2) classification of water according to a pollution level;
- 3) analytical information distributed to interested parties that is comprehensive and hands-on [2].

The method of complex evaluation of a pollution level of surface water according to the hydrochemical indices in order to generalize information about the chemical composition of water proposes an algorithm of calculating a combinatorial index of water pollution and combinatory pollution effect that constitutes an overall pollution level and specific combinatory water pollution index.

The latter is used to assess the proportion of a pollution effect that makes up an overall pollution level that involves a combination of pollutants.

The result is the classification of water quality based on this index that allows surface water to be classed into 5 groups depending on their pollution level: the first class is relatively clean, the second one is slightly polluted, the third one is polluted, the fourth one is dirty, the fifth one is extremely dirty.

The value of a specific combinatory water pollution index might vary from 1 to 16 in water with different pollution levels. The worst water quality corresponds with a large index. Currently calculations of these indices are top priority for evaluating a pollution level (quality) of water as unlike a combinatorial index of water pollution, apart from determining a multiplicity of an increase over MPC as well as recurrent increases, these indices are more indicative of the actual water quality.

Only hydrochemical indices are taken into account as well as for calculations of a combinatorial index of water pollution [2].

The objective of the paper is to identify the pollution level of water reservoirs that are located in the vicinity of an ore-mining plant. A complex evaluation of a pollution level of surface waters according to the hydrochemical indices was performed in compliance with the Guideline 52.24.643-2002.

1. Research methods. Samples of river water in the vicinity of an ore-mining plant were taken for the study. The samples were being collected in two sites over four months. Site № 1 is up the stream, Site is lower with several rivers flowing between them. The character and intensity of the *smell* of natural water, clarity were determined according to the Guideline 52.24.496-2005.

For determining the chemical indices of natural water: a dry residue, pH, ions of iron, manganese, copper, zinc, ammonium, nitrate-, nitrite-, chloride-, phosphate- and sulfate ions, chemical consumption of oxygen, biological consumption of oxygen over 5 days, the methods of gravimetry, photometry, turbidity, titrimetry were employed according to the methodology of quantitative chemical analysis (Table 1).

Table 1

Set of methods of Natural Federal Guidelines (NFG) adopted for the state
and industrial environmental control of nature preservation

1	pH	NFG 14.1:2:3:4.121-97	9	Nitrate-ion	NFG 14.1:2.4-95
2	Clarity	Guideline 52.24.496-2005	10	Nitrite-ion	NFG 14.1:2.3-95
3	Smell	Guideline 52.24.496-2005	11	Ammonium ion	NFG 14.2:4.209-05
4	Chlorides	NFG 14.1:2.96-97	12	Phosphate-ion	NFG 14.1:2.112-97
5	Sulfates	NFG 14.1:2.159-2000	13	Biological consumption of oxygen over 5 days	NFG 14.1:2:3:4.123-97
6	Iron	NFG 14.1:2.2-95	14	Chemical consumption of oxygen	NFG 14.1:2.100-97
7	Copper	NFG 14.1:2.48-96	15	Dry residue	NFG 14.1:2.114-97
8	Zinc	NFG 14.1:2.60-96	16	Manganese	NFG 14.1:2.61-96

2. Analysis of the determined physical and chemical characteristics of natural river water. Table 2 presents the results of determining the physical and mechanical characteristics of the investigated samples of river water compared to the guidelines for water objects of fishing water use.

A hydrogen index is essential to the character of chemical and biological processes occurring in water. Depending on pH, the rate of chemical reactions as well as corrosion aggression, toxicity of pollutants, etc. might vary. According to the classification of natural water based on a hydrogen index, the investigated sample is alkaline over the entire time range (pH from 7.5 to 7.9), except November when pH of water can be called neutral (pH from 7.1 to 7.3).

It was found that among the examined characteristics an increase in the MPC is seen in iron, copper, manganese as well as chemical consumption of oxygen as well as biological consumption of oxygen over 5 days (Fig. 1). This was the case for iron and copper throughout the entire study. An increase in the MPC for the biological consumption of oxygen over 5 days occurred only once below the flow in December, which is likely due to seasonal changes [9]. The iron content was 6.8 of MPC at the beginning of autumn and 1.8 of MPC at the beginning of winter. There is a reduction in the iron content in the run up to December.

Iron coming into surface water is largely due to weathering of rock and its subsequent solution as well as anthropogenic pollution also by waste water of ore-mining plants. Surface water contains iron as an impurity mainly in organic complexes with humic acids and it also forms colloid and high-dispersion dredge. At $\text{pH} > 4.5$ iron (II) is oxidized to iron (III) that precipitates into a hydroxide [7]. A high concentration of iron at these sites might be due to a fairly high natural level of iron in this area, however one cannot eliminate the technological factor altogether.

Table 2

Concentration of pollutants in natural surface water (September-December 2016)

Determined characteristics	Standrad MPC	September		October		November		December	
		Site 1	Site1	Site 2	Site1	Site1	Site 2	Site 1	Site 2
pH	6.5—8.5	7.5	7.5	7.8	7.9	7.3	7.1	7.5	7.5
Clarity, cm	No less than 10	15.2	17	27.5	21	18.0	15.0	25.2	26.3
Smell, point	No more than 2	0	0	0	0	0	0	0	0
Dry residue, mg/dm ³	1000	107±20	102±19	98±19	119±23	166±32	129±25	121±23	133±25
NH ₄ ⁺ , mg/dm ³	0.5/0.39	Less than 0.05							
NO ₂ ⁻ , mgdm ³	0.080	0.025±0.006	0.023±0.006	0.041±0.010	0.033±0.008	Less than 0.02	Less than 0.02	Less than 0.02	0.022±0.006
NO ₃ ⁻ , mg/dm ³	40	Less than 0.1	Less than 0.1	0.12±0.02	1.38±0.24	0.42±0.08	0.39±0.07	0.37±0.07	0.35±0.06
SO ₄ ²⁻ , mg/dm ³	100	4.9±1.0	5.2±1.0	7.3±1.5	13.1±2.6	8.6±1.7	8.3±1.7	8.0±1.6	7.8±1.6
Total amount of iron mgdm ³	0.1	0.68±0.136	0.69±0.14	0.38±0.076	0.60±0.12	0.26±0.052	0.24±0.048	0.18±0.036	0.18±0.036
Copper, mgdm ³	0.001	0.0033±0.0018	0.0027±0.0015	0.0027±0.0015	0.0048±0.0026	0.0039±0.0020	0.0053±0.0016	0.0053±0.0016	0.0028±0.0015
Zinc, mgdm ³	0.010	0.0089±0.0031	0.031±0.011	0.010±0.0035	0.029±0.010	0.078±0.028	0.036±0.013	0.013±0.005	0.010±0.0035
Mangnese, mg/dm ³	0.010	0.012±0.003	0.014±0.004	0.013±0.004	0.024±0.008	0.028±0.008	0.019±0.007	Less than 0.01	Less than 0.01
Chemical consumption of oxygen, mg/dm ³	No more than 15	41.0±9.8	32.0±7.7	11.0±2.6	22.0±5.3	34.0±8.2	36.0±8.6	9.0±2.7	8.0±2.4
Biological consumption of oxygen over 5 days days	No more than 2.0	1.28±0.33	1.45±0.38	0.85±0.22	0.88±0.23	1.17±0.30	2.3±0.60	Less than 0.5	0.81±0.21
Cl ⁻ , mg/dm ³	300	1.54±0.25	1.82±0.29	1.31±0.21	1.77±0.28	48.0±5.3	8.8±1.4	Less than 1.0	Less than 1.0
PO ₄ ³⁻ , mg/dm ³	0.61	Less than 0.05							

The content of copper in natural fresh water ranges from 2 to 30 mkg/dm³ [5]. The major source of copper in natural water is waste water of chemical and metallurgical industry, mines as well as aldehyde reagents used for destroying weeds. Copper might occur due to copper pipelines and other structures employed in water supply systems [13].

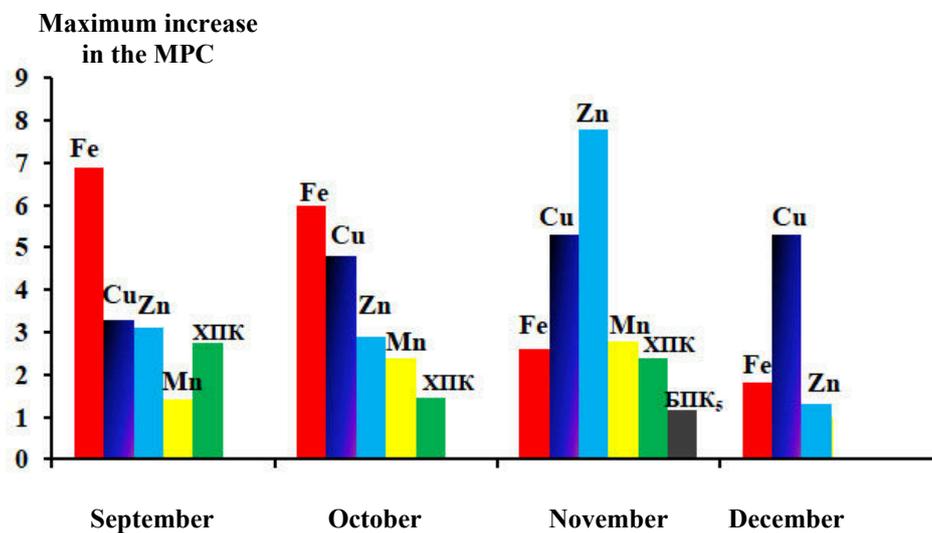


Fig. 1. Maximum increase in the MPC of pollutants over the examined period

Apart from natural sources of zinc in natural water such as failure and solution of rocks and minerals, one of the technological sources of zinc is waste water of an ore-mining plant. In all the investigated samples there is an increase in the MPC of copper from 3.3 to 5.3 of the MPC and zinc from 1.3 to 7.8 of the MPC. A considerable increase in the concentration of these elements compared to the MPC is most likely due to technological effects on the water quality.

Natural sources of manganese in surface water are leaching of iron manganese ores and other minerals containing manganese as well as decomposition of water organisms of herbal and animal origin. Alloys of manganese are washed into water reservoirs with waste water of manganese mining plants, metallurgic plants, chemical industry plants and mines [10].

The data analysis showed that natural water has a high manganese content as well as iron alloys. Increases in the concentrations of up to 1.4—2.8 of the MPC in the samples indicate that there might be a technological impact. Chemical consumption of oxygen is proved by significant and expected seasonal changes. In the investigated samples there was an increase in the MPC of 1.5 to 2.7, which might be due to a high content of organic substances coming into water with surface waste as well as household and industrial waste water.

3. Calculation of specific combinatory index of water pollution. According to the method adopted in the guidelines for objects of fishing water use, the indices of complex evaluation of a pollution level of the investigated water sample were calculated. Change in the coefficient

of the complexity is presented in Fig. 2. Note that the largest complexity of a pollution level is found in November, which indicates an increase in the effect of an anthropological factor on the water quality.

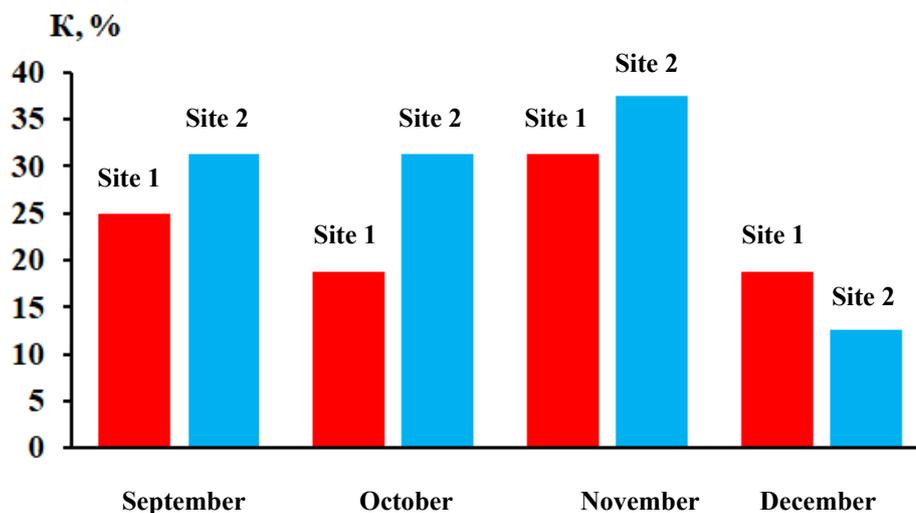


Fig. 2. Oscillations in the coefficient and complexity over the examined period

Due to a high coefficient of complexity ($K \geq 10\%$), a combinatory index of a pollution level is calculated. Table 3 and 4 present the indices that are over the MPC.

Table 3

Calculation of a combinatory index of a pollution level in Site № 1

Determined characteristics	n'_i	n_i	$\alpha = \frac{n'_i}{n_i} 100\%$	S_α	$\bar{\beta}_i = \frac{\sum \beta_i = \sum_i \frac{C_i}{\Pi \Delta K_i}}{n_i}$	S_β	S_i
Total iron, mg/dm ³	4	4	100	4.0	3.75	2.22	8.88
Copper, mg/dm ³	4	4	100	4.0	3.80	2.23	8.90
Zinc, mg/dm ³	2	4	50	4.0	4.55	2.32	9.28
Manganese, mg/dm ³	3	4	75	4.0	1.77	1.77	7.06
Chemical consumption of oxygen, mg/dm ³	2	4	50	4.0	2.50	2.06	8.25

Note: n'_i is the number of the results of a chemical analysis for the i -th ingredient in the solution over the examined period where their content is over the MPC; n_i is the total number of the results of a chemical analysis over the examined period for the i -th ingredient; α are recurrent pollutions; S_α is a particular evaluation point; β_i is the multiplicity of an increase in the MPC; $\bar{\beta}_i$ is an average multiplicity of an increase in the MPC; S_β is a particular evaluation point; S_i is a generalized evaluation point.

Calculation of a combinatory index of a pollution level of the water in Site № 2

Determined characteristics	n'_i	n_i	$\alpha = \frac{n'_i}{n_i} 100 \%$	S_α	$\bar{\beta}_i = \frac{\sum \beta_i = \sum \frac{C_i}{PDK_i}}{n_i}$	S_β	S_i
Total iron, mg/dm ³	4	4	100	4.0	4.28	2.84	11.36
Copper, mg/dm ³	4	4	100	4.0	3.90	2.24	8.95
Zinc, mg/dm ³	3	4	75	4.0	3.20	2.15	8.60
Manganese, mg/dm ³	3	4	75	4.0	1.90	1.90	7.60
Chemical consumption of oxygen, mg/dm ³	3	4	75	4.0	2.00	0.00	0.00
Biological consumption of oxygen over 5 days	1	4	25	2.8	1.15	1.15	3.16

According to the number of recurrent pollutions α , for the first site *stable pollution* is typical in all the indices that are over the MPC (copper, iron, copper, zinc, manganese, chemical consumption of oxygen). For the second site the identical indices supplement *unstable pollution* in the biological consumption of oxygen over 5 days.

According to the multiplicity of the MPC, a pollution level is characterized as *high*. According to the obtained specified combinatory pollution level index (for Site № 1 — 2.648 and Site № 2 — 2.480), it was found that the investigated water sample belongs to the third class, type — b: very polluted.

Conclusions

1. The dynamics of changes in the water quality in the vicinity of an ore-mining plant in one of the periods of a high waste flow was studied. The main pollutants and the maximum coefficients of an increase in the maximum permissible concentration: zinc (7.8 of the MPC), iron (6.8 of the MPC), copper (5.3 of the MPC) that are stable over the entire period are identified. It was shown that the use of the method of complex evaluation makes it possible to utilize an objective index, i.e. a specific combinatory index of water pollution, which allows an environmental condition of water objects of different regions with different anthropogenic load to be compared.
2. The characteristics of the investigated river water in the vicinity of an ore-mining plant as being very polluted is determined. Based on the available data of state monitoring of environment of the region up to 2016, that did not deteriorate. It is obvious that the investigated surface water experiences a strong technological load and purifying equipment cannot handle

that, which further deteriorates due to the use of modern equipment where an isolated water supply circle is employed, which results in polluted water coming into a precipitation tank and after going through a purification cycle they continue to be used in a lot of technological processes where they are repeatedly polluted and thus pose an increasing threat. The data obtained allows one to predict deterioration of the surface water of our region during nickel mining in Novokhopersk region.

According to [8], plants in this country that specialize in mining and enriching sulfide ore have no experience of operating under demanding environmental requirements. Therefore during construction of an ore-mining plant it is necessary to consider a certain combination of factors that can be found e.g., in studies dealing with the perspectives of developing sulfide-cobalt-copper-nickel deposits in Novokhopersk region [17] as well as research in purification of waste and natural water by means of various methods, e.g., [1, 14, 15, 18—22].

It is also of equal importance to investigate a transfer of pollutions into a stable form that could be stored long-term or employed in different industries.

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