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INVESTIGATION OF SURFACE WATER QUALITY IN MAGNITOGORSK INDUSTRIAL AREA FOR THE ENVIRONMENTAL ESTIMATION OF TECHNOGENIC WATERCOURSE STATE

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Наведено геологічна характеристика промислового району, дана екологічна оцінка стану техногенних видатків та стану поверхневих вод р. Урал, схильних до впливу гірничо-збагачувального і металургійного виробництв ВАТ «ММК», м. Магнітогорськ, Росія (РФ). На основі аналізу ряду показників авторами показано зв'язок між характером промислових стоків і властивостями води (жорсткість, мінералізація, лужність, вміст хлоридів і сульфатів)

Ключові слова: промислові стоки, водневий показник, важкі метали, мінералізація, іригаційні показники

Приведена геологическая характеристика промышленного района, дана экологическая оценка состояния техногенных водотоков и состояния поверхностных вод р. Урал, подверженных влиянию горно-обогатительного и металлургического производств ОАО «ММК» г. Магнитогорск, Россия (РФ). На основе анализа ряда показателей авторами показана связь между характером промышленных стоков и свойствами воды (жесткость, минерализация, щелочность, содержание хлоридов и сульфатов)

Ключевые слова: промышленные стоки, водородный показатель, тяжелые металлы, минерализация, ирригационные показатели

1. Introduction

Magnitogorsk Iron and Steel Works OJSC, Magnitogorsk, Russian Federation, is one of the world's largest steel producers representing a large metallurgical complex with a full production cycle, starting with preparation of iron ore raw materials and finishing with in-depth processing of ferrous metals. Functioning of such a complex is impossible without negative environmental impact.

In this regard, study of environmental impact of dust emissions and industrial effluents on the state of surface waters of the Ural River and Magnitogorsk water storage reservoir, Magnitogorsk, Russian Federation, in the zone of influence of the mining and smelting metallurgical complex is a relevant task.

2. Literature review and problem statement

Article [1] has performed analysis of data on water quality for the local technical water supply system. In general, water was tested for content of such components as ammonium, iron, nitrites, zinc, copper, hexavalent chromium, manganese, oil products and suspended solids. The studies presented in this work were conducted for one year and therefore could not reliably assess water quality. Studies conducted for 3 to 5 years can be considered reliable. Paper [2] has shown that mining enterprises generate the largest negative impact on all environmental components: atmosphere, hydrosphere and lithosphere. Under current situation, when resources get depleted, there is a need for assessing the level of environmental safety of various mining and processing technologies. Currently, there are three ways to assess environmental safety of industrial enterprises. Assessment of environmental safety of industrial enterprises is done using an approach based on the principle of normalization [3], an approach based on the principle of ecological risk (or environmental damage) [4] and an ecological and economic approach based on the principle of an "integral criterion" [5]. The main shortcomings of these approaches [6] are explained by complications in the specific environmental review of the mining enterprises. Basic disadvantages of these approaches consist in the aggregate technology used by mining companies, difficulties in choosing the target solution and subjectivity in decision ranking. The work proposed a new approach to assessing safety and impact on environment using an integrated indicator of environmental hazards in the mining industry. The indicator is based on complex environmental, technological and geological factors. This approach allows one to assess mining companies from the point of view of reducing negative impact on environment and determine the most effective actions. The work focuses on all water bodies and not specifically on the Ural River [7]. Work [8] considers the issues of negative impact of metallurgical and mining enterprises of the Middle and Southern Urals on water resources. The pollutants characteristic for enterprises of the mineral-raw complex including ferrous and non-ferrous metallurgy and the enterprises extracting building materials were ascertained. Information was provided on pollution of water bodies with metals, nitrogen compounds, sulfates, manganese and other substances. The main sources of pollution and measures to reduce the negative impact on environment were considered.

The issue of wastewater reuse for irrigation in agriculture as one of the useful managerial methods for reducing scarcity of water resources in arid and semi-arid regions of China was considered in paper [9]. Industrial wastewater from the city of Shijiazhuang is discharged into the Vanyan River after its treatment. Water is used downstream in irrigation of agricultural land. The purpose of this study was to study how almost 20 years of irrigation with the Vanyan River water affected soil characteristics, labile organic C soil and soil enzyme activity and compare the microbial response with a long-term irrigation in different locations of the riverside. The results showed that long-term irrigation with river water has led to accumulation of Hg, Cd, As, Pb, Cu, Cr, Zn and Mn in the underlying soils [9].

Reuse of wastewater is considered worldwide as an essential element of sustainable water resource management. Dissolved organic matter (dEfOM) present in biologically treated urban wastewater consists of a heterogeneous mixture of refractory organic compounds of various structures and origins. In particular, dissolved natural organic matter, soluble microbial products, endocrine damaging compounds, pharmaceuticals and personal care products, disinfection by-products, metabolite transformation products, etc. that can penetrate the aquatic environment because of the use of discharges and their reuse have to be mentioned. Efficiency of various advanced processing processes (e. g. membrane filtration and separation processes, adsorption of activated carbon, ion exchange resin process and advanced chemical oxidation processes) when dEfOM is removed from wastewater was evaluated in work [10]. Typically, the published data show that removal of dEfOM by advanced processing methods depends on the type and amount of organic compounds present in the aqueous matrix as well as on the operating parameters and removal mechanisms in application of each treatment technology [10].

Article [11] considers environmental pollution by textile dyes along with wastewater. Textile dyes and effluents are among the most serious pollutants of our valuable water bodies and soils. They are well known mutagenic, carcinogenic, allergic and cytotoxic agents posing threat to all life forms. Work [12] asserts that the effective restoration and reuse of the huge amount of agricultural and food waste generated daily can improve sustainability of food production systems. Anaerobic digestion (AD) is used worldwide as a waste treatment process to convert organic waste into two main products: biogas and a nutrient-rich hydrolyzate called AD wastewater. Biogas can be used as a source of renewable energy or transport fuels while AD wastewater is traditionally introduced to the soil as a supplement.. However, there are economic and environmental problems limiting widespread use of land, which can lead to underutilization of AD for processing agricultural and food waste. To combat these limitations, new methods have emerged for treatment or reuse of AD wastewater. The purpose of this review is to analyze several new methods used for the effective treatment and reuse of AD wastewater. In general, application of new technologies is limited by composition of AD wastewater, especially by high solid matter content. Some technologies, such as composting, use solid fraction of the AD effluent while most other technologies, such as algae growth and struvite crystallization, use liquid fraction. Therefore, AD wastewater dehydration, reuse of liquid and solid fractions and soil utilization can be combined for a sustainable management of large volumes of the produced AD wastewater. Current issues such as regeneration of pathogenesis and the extent to which emerging organic micropollutants have spread are discussed as well.

Review of the published data concerning the presented problem showed that a study of the surface water quality in the Magnitogorsk industrial region is of fundamental importance for ecological state assessment of the regional technogenic watercourses. Water is one of important components of life support for people regardless of geographic location of the region or country. The obtained results can be applied for those territories where there are developed metallurgical complexes.

3. The study objective and tasks

This work's objective was to study quality of surface waters in the Magnitogorsk industrial region for the ecological assessment of state of technogenic watercourses for their subsequent use.

To achieve this goal, the following tasks were set:

– investigation of technogenic watercourses for the content of heavy metals;

– determination of irrigation indicators and use of pond water for irrigation.

4. Material and methods for the study of technogenic watercourses

The city of Magnitogorsk is characterized by a high developed industry, in particular metallurgy which adversely affects ecological situation in the region.

Anthropogenic load on the environment within the city is very heavy: the volume of industrial waste per person is about 40 tons/year. Pollutant emissions into atmosphere are as high as 17.4 tons/year (2016). Water consumption in the city (household, drinking and production) is from 30 to 40 million m^3/year, the rate of contaminated water discharge into surface water is 11.36 million m^3/year (2016). The highest ecological load on the Ural River is 33 tons per 1 km.

This region climate is sharply continental with a long cold winter and a short but warm summer. The amount of precipitations is 140–250 mm per year.

The average annual air temperature is +3 °C.

The average temperature in winter is –16 °C.

The average air temperature in summer is +19 °C.

South-west winds prevail in the winter season and western, north-western winds in the summer season.

The average wind velocity is 3.5 m/s.

The height of the snow cover is from 0.23 to 0.66 m.

The frost penetration reaches 1.5–2.0 m for bare soil and 1.0–1.5 m for soil under a deep snow cover.

A characteristic feature of the geological structure of the region [13, 14] is monoclinic fall of rocks to the west and south-west at an angle of 15–20°, presence of numerous fracture zones and a powerful, nonconstant along the crust extension weathering of volcanogenic and volcanogenic-sedimentary rocks of the Visean stage of the Carboniferous system.

Natural water-bearing horizons are confined to gravel-flint sediments of channel alluvium and to fractured differences of bedrocks. The alluvial water-bearing horizon is characterized by pressure equal to 1.5–5 m above the level of the formation roof. Alluvial loams and deluvial-proluvial deposits with a filtration coefficient of 0.1 m/day serve as a water-pressure roof.

In general, the region is dominated by a cracked vein type of water. Waters by their zoning belong to the Upper Urals mesobasin of the Ural drainage macro basin. At the same time, the right bank of the Ural River is characterized by hydrocarbonate, hydrocarbonate-sulfate underground waters with a 1–1.5 l/s km^2 interflow module. Hydrocarbonate, hydrocarbonate-chloride waters with an interflow module less than 1 l/s km^2 are characteristic for the left bank. The average chemical indexes of water (ml/l) are as follows. Mineralization: 760, chlorides: 73, sulfates: 54, water pH: no more than 8.

Given these figures of the groundwater quality in the area, it can be asserted that the overall resistance of natural water to pollution is low. A very low module of interflow increases pollution vulnerability of water.

Under the conditions of localization of contaminated production waste in the Earth interior, the region is considered unreliable. It is recommended to use limited areas to localize non-conservative contaminant components in the areas of geochemical barriers.

To study the state of surface waters, water from the Ural River and the regional technogenic watercourses were tested. Water samples were taken monthly during 2008–2010 from the main technogenic watercourses (samples 401–406), the Ural River and the Magnitogorsk Reservoir (samples 501–519). Sampling of natural and waste water was carried out in accordance with the requirements of GOST R 515925, GOST 17.1.5-05, SanPiN (Sanitary Regulations and Code) 2.1.5.980 and RD 52.24.353.

Samples were taken from turbulent, well-mixed flows on rectilinear sections of the drainage devices outside the action of heading-up. The layout of the sampling points shown in Fig. 1 was planned in such a way as to reveal the nature of impact of the left-bank part of the reservoir, which adjoins the industrial site of the plant on the quality of surface waters. Taking into account the high importance of the Ural River, water sampling was done over a stretch of 40 km from the dam of the Verkhneuralsk reservoir (sample 501) to Agapovka village (sample 519).

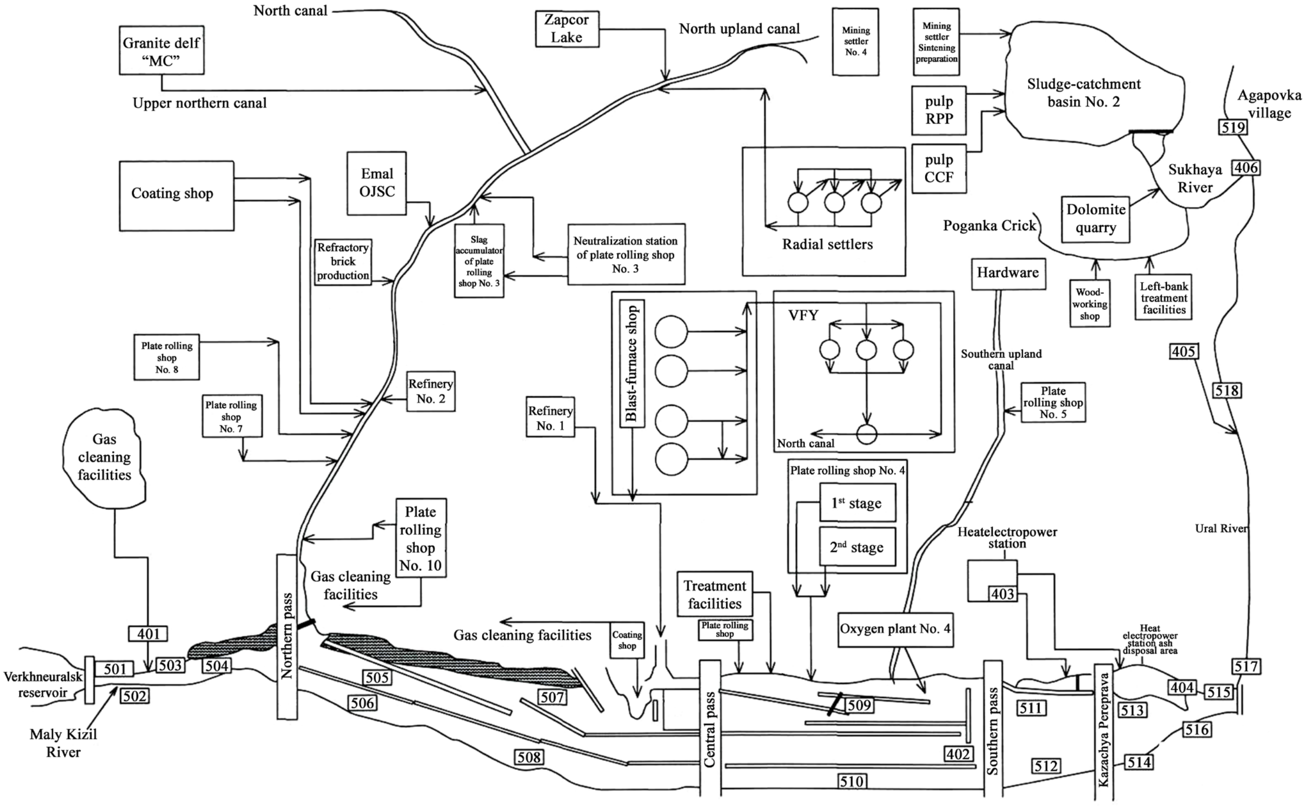


Fig. 1. Sketch map of sampling locations

The water samples were tested for ionic composition, metals and suspended matters. Concentration of metals in the samples was determined by the method of atomic absorption spectroscopy using a Kvant-Z ETA device (Russian Federation). The water samples were tested for Ni, Si, NH_4^+ by spectrophotometric method, Cl^- was determined by tetrametric and gravimetric methods. Alkalinity was determined by tetrametric method with potentiometric indication of the equivalence point. The content of petroleum products was determined by fluorimetric method.

Irrigation indicators were calculated by empirical methods proposed in [15] and by the US Department of Agriculture (SAR indicator) [11].

According to the method of [15], a number of coefficients for calculating water suitability for irrigation were determined:

– with mineralization of water less than 1 g/l:

$$K_1 = [Na^+]/[Ca^{2+}] \text{ (for irrigation water } \leq 1), \quad (1)$$

$$K_2 = [Na^+]/([Ca^{2+} + Mg^{2+}]) \text{ (for irrigation water 0.7 [15])}. \quad (2)$$

The value of ion exchange [15] was calculated using the formula:

$$K = ([Ca^{2+}]+[Mg^{2+}])/[Na^+]+0{,}238S, \quad (3)$$

where S is water mineralization (g/l).

Water is considered suitable for irrigation if K>1 and unsuitable if K≤1.

The Steebler (K_a) irrigation coefficient for various chemical types of water was calculated using the following formulas:

$$K_a = 288/5[Cl^-] \text{ at } [Na^+]<[Cl^-], \quad (4)$$

$$K_a = 288/[Na^+]+4[Cl^-]$$

at

$$[Cl^-]+[SO_4^{2-}]>[Na^+]>[Cl^-], \quad (5)$$

$$K_a = 288/(10[Na^+]+5[Cl^-]-9[SO_4^{2-}])$$

at

$$[Na^+]>[Cl^-]+[SO_4^{2-}]. \quad (6)$$

Quality of irrigation water is considered good if K_a>18, satisfactory if K_a=18–6, unsatisfactory if K_a<1.5. In the investigated case, coefficient K_a was calculated by formula (4).

Potential sodium absorption ratio (*SAR*) was calculated by the formula:

$$SAR = [Na^-[/\sqrt{([Ca^{2+}]+[Mg^{2+}])/2}. \quad (7)$$

Proceeding from the SAR, probability of alkalinization is considered low if SAR<10.

By the ratio between monovalent cations and the sum of cations [15]:

– very unfavorable for irrigation:

$$([Na^+]+[K^-])/([Ca^{2+}]+[Mg^{2+}]+[Na^+]+[K^+])>75\,\%, \quad (8)$$

– unfavorable for irrigation:

$$([Na^+]+[K^-])/([Ca^{2+}]+ +[Mg^{2+}]+[Na^+]+[K^+])=66-75\,\%, \quad (9)$$

– favorable for irrigation:

$$([Na^+]+[K^-])/([Ca^{2+}]+[Mg^{2+}]+[Na^+]+[K^+])<66\,\%. \quad (10)$$

In addition, it was found that in assessing quality of irrigation water, along with the share of monovalent cations, pH is an important indicator. According to the pH value, three types of water are distinguished: acid (pH less than 6.5), neutral (pH=6.5–8.0) and alkaline (pH more than 8). A noticeable increase in alkalinization occurs when pH of the irrigation water is 8–8.5.

The ion exchange indicator was calculated by the formula:

$$K = ([Ca^{2+}]+[Mg^{2+}]/([Na^+]+0{,}238S), \quad (11)$$

where S is water mineralization (g/l).

Water is considered suitable for irrigation if K>1 and unsuitable if K≤1.

All abovementioned indicators were calculated in mg-equ./l.

5. Results of studies of surface water quality in the Magnitogorsk industrial region

Formation of the chemical composition of water. Coming of industrial effluents from the ore-dressing and metallurgical integrated works has led to a significant change in the physicochemical parameters of the aquatic environment [16]. Chemical composition parameters of the main technogenic watercourses from the works are presented in Table 1, 2 (averaged values for 2008, 2009 and 2010).

The greatest influence on concentration of components of the chemical composition of water was exerted by industrial wastewater of the Northern and Southern upland canals as well as industrial wastes from the limestone quarry and via the Sukhaya River from the ore mining and processing enterprise. E. g., the discharge from the limestone quarry in the Agapovka area (sample 405) was characterized by an elevated hydrogen index (pH=9.83) as well as a high magnesium content (31.71 mg/l), mineralization (>1 g/l) and elevated iron content (over 2 MPC), manganese (13 MPC), copper (more than 3 MPC), zinc (more than 3 MPC). Also, an increased content of sulfate ions (314 mg/l) and phosphate ions (1.15 mg/l) was characteristic this water. Excess of suspended particles was as high as 3 MPC.

The technogenic watercourse from the ash and rock sludge pond in the vicinity of Mokhnataya town, Magnitogorsk region, Russia (sample No. 401) was also characterized by an elevated hydrogen index (pH=94), an elevated content of phosphate ion (3.5 mg/l) and suspended particles (80 mg/l). The excess for iron was 2 MPC, and 3 MPC for zinc. The watercourse of the Sukhaya River (sample 406) was characterized by a high content of magnesium (21.38 mg/l) and mineralization (>1 g/l). There was a high content of iron, manganese (more than 6 MPC), copper (1.5 MPC), zinc 7 MPC. The increased content of sulfate ions (394 mg/l) and phosphate ions (2.48 mg/l) was also characteristic for this area.

Besides, there was an aerotechnogenic transport of substances and removal of elements from the bodies of metallurgical production slag dumps by surface water. The existing wastewater treatment system efficiently reduces concentration of suspended Fe, Mn, Zn, Cu particles. However, sedimentation of suspended particles in a form of slime takes place on the bottom of sedimentation canals (in the mouth of the Severnaya upland canal and in the Levoberezhny sedimentation basin). Later on, slurry is dredged into slurry-catchment basins. Currently, more than 3 million tons of slurries with iron content of 50 to 70 % have been accumulated in the operating and stored slurry-catchment basins.

In general, as concerns the technogenic watercourses, it can be said that the hydrogen index exceeds figure of 8.5. What is characteristic, there are increased and high contents of iron, manganese, zinc, increased content of sulfate, phosphate and fluoride ions. Naturally, this affects quality of the surface waters of the Ural River and Magnitogorsk reservoir. The negative impact of technogenic waters of the metallurgical integrated works was traced down to Agapovka willage where elevated levels of iron, manganese, copper, zinc were found in comparison with the waters north of Magnitogorsk city [16].

Tables 3–6 present results of chemical analyzes of hydrochemical samples from the Ural River and Magnitogorsk reservoir.

Table 1

Results of chemical analysis of hydrochemical samples taken from technogenic waterways of the works

Components	Sample number					
	401	402	403	404	405	406
pH	9.94	8.76	8.72	9.40	9.83	8.34
Alcalinity, mol/l	1.44	3.07	3.19	3.30	4.76	3.35
Cl^-, mg/l	391.4	101.2	89.2	67.7	136.7	115.6
SO_4^{2-}, mg/l	167	14	128	153	314	394
v, mg/l	0.056	0.12	0.24	0.27	0.058	2,48
F^-, mg/l	6.19	2.35	1.15	1.31	1.15	1.49
NH_4^+, mg/l	2.19	1.99	0.39	0.43	0.18	0.15
Mg^{2+}, mg/l/mole/l	8.15/1.35	9.78/1.53	11.23/1.86	13.59/2.12	31.78/5.25	31.38/3.54
Ca^{2+} mg/l/mole/l	27.97/2.79	39.38/3.93	32.06/3.20	33.37/3.33	63.63/6.35	68.07/6.67
suspensions, mg/l	80	21	23	23	17	26

Table 2

Content of heavy metals in hydrochemical samples of technogenic watercourses of the works

Components	Sample number					
	401	402	403	404	405	406
pH	9.94	8.76	8.72	9.40	9.83	8.34
Fe, mg/l	0.94	0.61	0.55	0,72	0.23	0.66
Mn, mg/l	0.12	0.26	0.12	0.17	0.13	0.065
Cu, mg/l	0.022	0.0085	0.0046	0.0075	0.0031	0.0064
Zn, mg/l	0.52	0.63	0.17	0.037	0.036	0.070
Ni, mg/l	0.0056	0.0066	0.0022	0.0063	<0.005	<0.005
Pb, mg/l	0.0031	0.0042	<0.002	<0.002	<0.002	<0.002
Cd, mg/l	<0.00012	<0.00012	<0.00012	<0.00012	<0.00012	<0.00012
Si, mg/l	3.23	3.85	3.36	3.60	4.61	6.24
Mineral oils	0.12	0.38	0.17	0.15	0.058	0.075

Table 3

Content of heavy metals in hydrochemical samples taken from the Ural River and Magnitogorsk reservoir (pH, Fe, Mn, Cu, Zn)

Sample number	Components				
	pH	Fe	Mn	Cu	Zn
		mg/l	mg/l	mg/l	mg/l
501	8.16	0.26	0.16	0.0058	0.012
502	8.46	0.33	0.093	0.0032	0.02
503	8.40	0.38	0.11	0.0029	0.018
504	8.46	0.47	0.5	0.0030	0.026
505	8.95	2,09	0.13	0.011	0.24
506	8.29	0,39	0.13	0.0031	0.015
507	8.40	1,12	0.16	0.0062	0,45
508	8.22	0,38	0.12	0.0029	0.11
509	8.17	1.03	0.11	0.011	0,96
510	8.19	0,36	0.12	0.0023	0.083
511	8.2	0.11	0.09	–	–
512	8.4	0.24	0.10	0.0021	0.11
513	8.47	0.46	0.11	0.0032	0.14
514	8.92	0.68	0.10	0.0027	0.032
515	8.84	0.26	0.090	0.0040	0.033
516	9.11	0.22	0.074	0.0037	0.032
517	8.59	0.34	0.073	0.0086	0.063
518	8.93	0.25	0.059	0.0054	0.038
519	8.85	0.27	0.087	0.0029	0.049

Table 4

Content of heavy metals in hydrochemical samples taken from the Ural River and Magnitogorsk reservoir (Ni, Pb, Cd, Si, oils)

Sample number	Components				
	Ni	Pb	Cd	Si	Oils
	mg/l	mg/l	mg/l	mg/l	mg/l
501	0.0059	<0.002	<0.00012	2.91	0.091
502	0.0069	<0.002	<0.005	2.62	0.042
503	0.0055	0.11	<0.00012	2.58	0.041
504	0.0074	<0.002	<0.00012	2.91	0.051
505	<0.005	<0.002	<0.00012	4.32	1.62
506	0.0061	<0.002	<0.00012	3.01	0.056
507	0.0089	0.0058	<0.00012	3.13	0.4
508	0.005	<0.002	<0.00012	2.82	0.093
509	0.0011	<0.002	<0.00012	3.95	0.91
510	0.0054	<0.002	<0.00012	2.61	0.0097
511	0.0032	<0.002	<0.00012	1.21	0.063
512	0.0053	<0.002	<0.00012	1.54	0.071
513	0.0021	<0.002	<0.00012	2.37	0.15
514	0.0032	<0.002	<0.0012	1.47	0.13
515	0.0019	<0.002	<0.00012	2.01	0.11
516	0.0022	<0.002	<0.00012	1.67	0.16
517	0.0056	0.0023	<0.00012	2.01	0.12
518	0.0054	<0.002	<0.00012	2.57	0.11
519	0.0052	<0.002	<0.00012	2.53	0.064

Table 5

Results of chemical analysis of hydrochemical samples taken from the Ural River and Magnitogorsk Reservoir (pH, Cl^-, SO_4^{2-}, HCO_3^-)

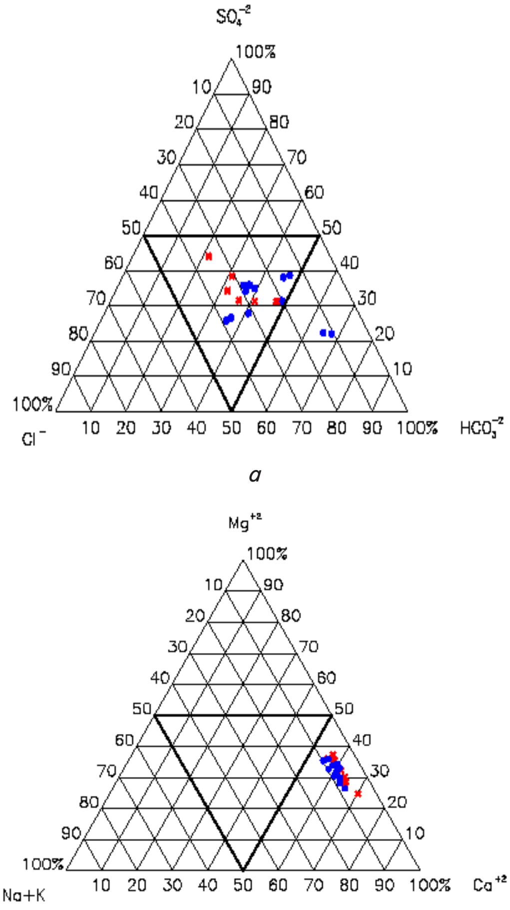
Sample number	Components			
	pH	Cl^-	SO_4^{2-}	HCO_3^-
		mg/l/mg-equ./l	mg/l/mg-equ./l	mg/l/mg-equ./l
501	8.16	14.0/0.4	36/0.75	140.7/2.31
502	8.46	15.8/0.45	37/0.77	134.3/2.20
503	8.40	19.8/0.57	83/1.73	128.1/2.10
504	8.46	24.7/0.71	79/1.65	119.3/1.96
505	8.95	110.6/3.16	201/4.19	120.4/1.97
506	8.31	21,2/0,61	77/1.6	121.2/1.98
507	8.40	106,4/3,04	181/3.77	183.3/3.00
508	8.22	7,31/2,09	71/1.48	124.7/2.04
509	8.17	109.7/3.13	149/3.10	179,5/2,94
510	8.19	53.2/1.52	67/1.40	119,7/1,96
511	8.2	58.2/1.66	89/1.85	141.6/2.32
512	8.4	78.4/2.24	72/1.5	125.6/2.06
513	8.47	70.3/2.01	98/2.04	137.2/2.25
514	8,92	59.1/1.69	88/1.83	118.7/1.95
515	8.84	32/0.91	63/1.31	126.1/2.07
516	9.11	61/1.74	98/2.04	116.2/1.91
517	8.59	31.6/0.90	63/1.31	125.5/2.06
518	8.93	65.3/1.87	113/2.35	161.7/2.65
519	8.85	71/2.3	151/3.15	198.0/3.1

Table 6

Results of chemical analysis of hydrochemical samples taken from the Ural River and Magnitogorsk reservoir (K^+, Na^+, Mg^{2+}, Ca^{2+}, Σ ions)

Sample number	Components				
	K^+	Na^+	Mg^{2+}	Ca^{2+}	Σ ions
	mg/l/mg-equ./l	mg/l/mg-equ./l	mg/l/mg-equ./l	mg/l/mg-equ./l	mg/l
501	2.4/0.06	2.3/0.1	7.01/0.58	22.64/1.13	225.05
502	1.9/0.05	2.2/0.09	7.19/0.60	21.01/1.03	219.4
503	1.8/0.05	2.4/0.1	7.61/0.63	19.74/0.98	262.45
504	2.2/0.06	2.6/0.11	8,09/0.67	32.74/1.61	268.63
505	20/0.05	3.1/0.13	10.27/0.85	48.04/2.36	495,41
506	1.9/0.05	3,3/0.14	8.39/0.69	30.16/1.51	263.15
507	1,8/0.05	3.4/0.15	10.83/0.89	41.98/2.09	528.71
508	2.30.06	2.4/0.1	8.65/0.72	29.76/1.49	311.91
509	2.5/0.07	2.4/0.1	10.30/0.81	34.27/1,71	487.67
510	2.3/0.06	2.9/0.12	8.52/0.71	24,89/1,22	278.51
511	2.1/0.05	2.0/0.09	10.15/0.84	24.75/1,24	327.8
512	2.0/0.05	1.9/0.08	9.54/0.79	27.15/1.36	316.59
513	2.1/0.05	1.8/0.08	9.82/0.81	30.36/1.52	349.58
514	1.9/0.05	2.0/0.09	9.38/0.77	29.96/1.49	309.04
515	1.8/0.05	1.9/0.08	9.85/0.81	22.75/1.34	257.4
516	1.9/0.05	2.0/0.09	9.54/0.79	29.36/1.47	318.0
517	2.0/0.05	2.1/0.09	8.88/0.74	22.85/1.14	255.93
518	2,5/0.07	2.3/0.1	10.75/0.89	32.36/1.62	387.91
519	2.5/0.07	2.00.09	12.44/1.03	37.17/1.86	474.21

According to the results of analysis of the water samples taken from the Ural River (Fig. 2) before the technogenic impact of the works (samples 401–402) according to the classification given in work [16], the water samples belonged to the first type of hydrocarbonate-calcium water. They are characterized by $HCO_3^- > (Ca^{2+} + Mg^{2+})$ in milligram-equivalent form and an increased pH value (>8.14), total mineralization did not exceed 1 g/l.



a

b

Fig. 2. Diagrams of chemical composition of the surface waters of the Ural River. *a* — outside the zone of technogenic impact of the works and the right bank of the reservoir; *b* — in the zone of influence of the works (left bank of the reservoir). × — Mg content; × — Ca content

In the zone of technogenic impact of the works (samples 403–419), water belongs to bicarbonate-sulphate-chloride (mixed) calcium water of the first type. In this case, it is necessary to point out different states of water in the Zavodskoy pond near the left bank (in the zone of influence of the works) and the right bank within the city of Magnitogorsk. The left bank is represented by ash-heaps with a good draining capacity, as well as effluents from Mohnataya sludge pond of ash and rocks, the northern canal of industrial wastewater and the sedimentation basin on the left bank [17].

A somewhat different pattern was observed in behavior of heavy metals. This 1.5–2 times increase in the content of iron, manganese and zinc in the Ural River from the Verkhneuralsk reservoir to Agapovka village, especially in the locations of discharge of technogenic water from the works. Water of the Zavodskoy pond near the left bank had maximum permissible concentration of iron, manganese (more than 2 MPC) and zinc, lead and nickel were at the MPC level. Iron content reached 2.23 mg/l in water taken from sedimentation tanks and slurry storage ponds of the works. Other figures were 0.18 mg/l for manganese, up to 0.96 mg/l for zinc, 0.28 mg/l for copper and 0.05 mg/l for nickel.

6. Discussion of the results obtained in the study of the watercourse chemistry

The data presented here indicate that the technogenic watercourses of the integrated metallurgical works have a negative impact on the of the Ural River water, especially in the Zavodskoy pond where elevated concentrations of heavy metals were found and cause changes in the chemical type of water, its main components. Negative impact of technogenic watercourses of the works can be traced to Agapovka village where elevated iron and zinc contents were found in comparison with the waters north of the city of Magnitogorsk.

Irrigation characteristics. The results of calculating irrigation parameters of the selected samples are shown in Table 7.

Table 7

Irrigation indicators of the tested water

Sample number	Irrigation indicators						
	pH	K_α	SAR	rNa+rK	K	K_1	K_2
501	8.6	144	0.11	8.56	287	0.09	0.06
502	8.46	128	0.10	7.91	347	0.09	0.06
503	8.40	101	0.11	8.52	261	0.10	0.06
504	8.46	8.1	0.10	6.94	325	0.07	0.04
505	8.95	17.9	0.10	5,31	210	0.06	0.04
506	8.31	92	0.13	7.95	251	0.09	0.06
507	8,40	19	0.12	6.30	158	0.07	0.05
508	8.22	27	0.09	6.75	298	0.07	0.05
509	8.17	17.2	0.09	6.32	217	0.06	0.05
510	8.19	38.4	0.12	8.53	242	0.10	0.04
511	8.2	35	0.09	6.31	296	0.07	0.04
512	8.4	26	0.08	5.70	356	0.07	0.04
513	8.47	29	0.07	5.28	350	0.05	0.03
514	8.92	34	0.08	5.83	341	0.06	0.04
515	8.84	63	0.08	5.70	439	0.06	0.04
516	9.11	33	0.08	5.83	332	0.06	0.04
517	8.59	64	0.09	6.93	343	0.08	0.05
518	8.93	30	0.09	6.34	272	0.05	0.04
519	8.85	25	0.06	5.25	284	0.04	0.03
Satisfactory indicators	<8.4	>18	<10	<66	>1	<1	<0.7

In general, the estimated irrigation indicators were in line with the norms. But within the bounds of the city (pond – cooler), water was characterized by an elevated pH (>8). Such pH value is already a limitation for the use of the pond water for irrigation purposes. It should be noted that water with a content of $CO_3 > 1.5$ mg-equ./l and pH>8.4 has limitations for irrigation of crops.

7. Conclusions

1. It was found that the content of heavy metals, in particular iron, manganese and zinc in the Ural River increases 1.5–2 times from the Verkhneuralsk reservoir to the Agapovka village. Especially this increase was noticeable at the locations of discharge of technogenic water from the works. Excess of maximum permissible concentration for iron and manganese (more than 2 MPC) and the level of MPC for zinc, lead, and nickel were found in the Zavodskoy pond water near the left bank. Iron content reached 2.23 mg/l and other figures were 0.18 mg/l for manganese, up to 0.96 mg/l for zinc, 0.28 mg/l for copper and 0.05 mg/l for nickel in the water samples from sedimentation tanks and slurry storage.

2. The calculated irrigation indictors comply with the norms. But within the city limits (pond – cooler), water was characterized by an elevated pH (>8). Such value of pH is already a limitation for the use of the pond water for irrigation purposes. It should be noted that water with a content of CO^3>1.5 mg-equ./l and pH>8.4 has limitations for irrigation of crops.

In conclusion, it can be said that the technogenic watercourses of the works exert negative impact on the quality of surface waters of the Urals River, especially in the Zavodskoy pond where elevated concentrations of heavy metals as well as changes in the chemical type of water for main components were found. Negative impact of technogenic watercourses of the works can be traced down to Agapovka village where elevated content of iron and zinc were found in comparison with the waters northward of Magnitogorsk.

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