EEET ECOLOGICAL ENGINEERING & ENVIRONMENTAL TECHNOLOGY

Ecological Engineering & Environmental Technology, 2025, 26(8), 187–202
https://doi.org/10.12912/27197050/207533
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Received: 2025.05.19
Accepted: 2025.07.17
Published: 2025.08.01

Patterns of changes in hydrochemical parameters of surface water massifs in the area of influence of a thermoelectric power station

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ABSTRACT

For a long time, thermal power plants (TPPs) have been a source of significant anthropogenic pressure on the environment. None of the natural components remains unchanged. The load on aquatic ecosystems, the creation of special conditions for hydrochemical processes, the formation of new connections and interdependencies between they require a detailed analysis of chemical, physical and biological data, modelling of various strategies and planning to understand the changes that have occurred and to analyse their dynamic scenario in the next years. The aim of the study is to analyse the long-term impact of typical Burshtyn TPP pollution on the water bodies around it and to track their spatial and temporal behaviour using statistical analysis in order to improve the environmental safety of the Dniester tributaries flowing through Rohatyn Opillya and to identify the opportunities for more efficient management of the hydrological system. The study analysed the content of pollutants in water samples collected during 1993–2024 from ten locations in the Burshtyn cooling reservoir (BCR), the Dniester River and the Hnyla Lypa River (HLR), which form a connected water system influenced by continuous work of the Burshtyn TPP. The statistical analysis confirmed a series of slow changes in the contents of Ca and Mg. Therefore, slow but monotonous dynamics in the changes of water quality in the connected hydrological system HLR & BCR & Dniester River during the last 30 years of a hydrochemical load by the Burshtyn TPP, has been confirmed by a detailed statistical analysis of data selected independently in recent years and of the data available from the open sources. The results confirm that the water system considered can be used as a model system for mathematical estimation of the technological harm, ecological safety and the self-restoration abilities of such systems.

Keywords: ecological safety, surface water pollution, thermal power plant.

INTRODUCTION

The National Security Strategy of Ukraine specifies the main threats to environmental security, which are complicated by the Russian-Ukrainian war that is the most extensive armed conflict in Eastern Europe after 1945. The environment suffers essentially from a wide spectra of military actions (Malyrska et al., 2024), such as military chemical pollutions, wildfires, flooding from the destruction of dams, scorched soils, the fields and forests burned down, and the ecosystems destroyed (Hryhorczuk et al., 2024). The main reasons of the increase in the pollutions detected in the air, water and soil are bombing and wildfires resulted in destruction of fuel storage, civil and industrial facilities, buildings and infrastructure, agricultural areas and national parks. Among the most vulnerable objects are TPPs and their water reservoirs (coolers), which are an integral part of the technological process of energy generation. An important environmental problem related to TPPs is the quantitative estimation of their impact on surface waters, which are the main source for circulating technical water supply. Long-term operation of TPP has a significant impact on the quantitative and qualitative indicators of water bodies. The anthropogenic pollutions from TPPs can interact with other types of anthropogenic and natural pollutions (Howladar, 2017). One of these facilities is the BCR on the HLR, (a left tributary of the Dniester river), created in 1965 to meet the needs of the burshtyn TPP. During the 60-year existence of the BCR, a water ecosystem was formed, which is constantly subjected to technogenic and anthropogenic stress. Burshtyn TPP has a negative impact on the environment. In 2009, Burshtyn was ranked as the third worst air quality city in Ukraine. After the Russian bombing on 22 March 2024, the units of Burshtyn plant were in different degrees of destruction: from complete to > 50%. Therefore, the problem requires detailed studies of air, soil, and water within the limits of TPP influence.

This study presents a retrospective analysis of the pollution level of the BCR from 1993 to 2024 and an analysis to predict the possibility of self-recovery of the water system and its environmental safety, taking into account the transfer and accumulation of pollution.

The following aspects of environmental pollutions attributed to TPPs are mainly discussed in literature:

1. Thermal pollutions which are determined as noticeable changes (increase or decrease) in the temperature of water, air and soils as a result of human activities (Glibovytska et al., 2024);
2. Soil contamination by fly ash and chemical products of combustion/burning (Kravchynskyi et al., 2021);
3. Chemical contamination of surface water (Matiyiv et al., 2022);
4. Groundwater contamination by ash and chemicals, and increase in its salinity (Klymchuk et al., 2022);
5. Air contamination by ash, chemicals (NO_x, SO_2, CO, CO_2, Ozone (O_3), Mercury (Hg), Lead (Pb) and other heavy metals, volatile organic compounds) and Particulate Matters (harmful microparticles) PM_{10} and $PM_{2,5}$ (Adamenko et al., 2024).

Thermal pollutions caused by industrial activity dominate in the world. The largest users of water for industrial cooling are electric power stations, and the temperature increase is a byproduct of electricity generation. The surface temperature of the territory is compared with environmental indices, as evidenced by the strong correlation between these indicators (Mokarram et al., 2023). The multiple linear regression (MLR) analysis revealed a strong correlation between the temperature and TOC, COD, and O_2 in water ($R_{TOC}{}^2 = 0.98$), ($R_{COD}{}^2 = 0.87$) and O_3, NO_3, CO_2, and CO in the air.

Some TPPs use seawater as the source and sink of cooling water (Lin et al., 2020). The heat production and temperature rise produced by heat pollution have negative influence on the plants and animals (Arieli et al., 2011) which prefer low and moderate temperatures (Xu et al., 2021), and occurs a positive influence of the heat-tolerant flora and fauna (Vallero, 2025). A cumulative effect of thermal discharge from power plants can produce long-term surface thermal plumes (Wei et al., 2023).

Soil contamination caused by fly ash from coal-fired TPPs has been studied in India that is the world's second-largest country in coal production and consumption (Luo et al., 2024). It was shown, the disposal, reclamation, and management of fly ash from TPPs must be regulated and monitored correctly to ensure the safety of its use. Similar problem was studied on pollutions by ash produced by combustion of heavy fuel oil in TPPs (Bady et al., 2024). In Turkey, a considerable part of air contamination by SO_2 is determined by lignites with higher amounts of ash, moisture, and sulphur which are used as fuel in the TPPs (Say, 2006). The ash produced by the coal-fired TPPs can be used in recycling technology that improves the environment (Koshlak, 2021).

The fly ash produced by TPPs and disposed in large ponds through their surface can also influence the quality of groundwater as it was shown by analyses of H_2 and O_2 isotopes (Voltaggio et al., 2015). In China, TPPs produce > 80% of generated electrical energy and discharged > 40% of NO_x and SO_2 (Tsai, 2022). The control and clear air management needs detailed statistical analysis of the relationships between the amounts of different pollutants and numerical modelling (Wang et al., 2010).

Atmospheric emissions from the coal-fired TPPs are responsible for a worsening of human health (Guttikunda and Jawahar, 2014). Many animals and plants are also very sensitive to specific pollutions. On the territories influenced by sulphur emissions from TPPs, the amount of total sulphur, photosynthetic pigments, ascorbic acid and α-tocopherol in current-year needles of Norway spruce (*Picea abies* L. *Karst*.) were changed

(Petkovsek et al., 2008). When the emission gases were desulfurized, the total sulphur content in needles decreased and vitality parameters of needles increased. Besides, installation of desulfurization systems in TPPs could reduce concentrations of the harmful microparticles $PM_{2,5}$ by 30–40% by eliminating the formation of the nitrates and sulphates (Guttikunda et al., 2014).

Therefore, TTPs working on combustion/burning of different types of fuels produce ash, vapour, chemical and organic pollutants that contaminate air, soils, surface and groundwater. Permanent monitoring and control over the quality of emission gases, discharges, temperature and pollutions of the technical water used for cooling of TTPs are very helpful for raising the ecological safety of TPPs. When the local ecosystem around a TPP is stable, the self-recovery of water, air and soil is observed. At the conditions of military activity with massive destroy of the power plants, reservoirs with fuels and chemicals, infrastructure and ecosystem, the pollution accumulation and synergy effect could make the self-restoration impossible. In this paper the problem of ecological safety of TTPs at the condition of military activity and its consequences are studied on the example of Burshtyn TTP.

MATERIALS AND METHODS

Location and hydrological parameters of the studied system BCR & HLR & Dniester River

According to (Directive 2000/60/EC of the European Parliament, 2000), it is appropriate to consider the peculiarities of the ecosystem of the HLR basin (Figure 1). The coordinates and descriptions of cites of water sampling are listed in Table 1. The considered ecosystem

Figure 1. Hydrological system BCR & HLR & Dniester River; the cites 1–10 of water sampling are marked by numbers; their coordinates and descriptions are listed in Table 1

Table 1. The coordinates and descriptions of the sites of water sampling

Site	Geographic coordinates	Description
1	49.263847, 24.642158	HLR; the place where the river flows into the BCR near Burshtyn town; local highway, recreational area, flat terrain
2	49.247770, 24.659238	left bank of the BCR; 2.5 km from the confluence of the river into the reservoir, village of Korostovichi; agricultural use of the territory, steep slope towards the reservoir
3	49. 233704, 24.666448	left bank of the BCR; 4.5 km from the confluence of the river into the reservoir, village of Korostovichi; agricultural use of the territory, forest landscapes, flat terrain
4	49.253568, 24.643531	right bank of the BCR; 4 km from the confluence of the river into the reservoir, village of Korostovichi; recreational area for residents of Burshtyn, sandy beach, flat terrain
5	49.20943, 24.68919	middle of the BCR dam near Burshtyn town; highways, flat terrain
6	49.271352, 24. 639154	HLR; 1 km before the river flows into the reservoir; coastal vegetation, shrubs, reeds, flat terrain
7	49.352769, 24.611002	HLR; 10 km to the BCR, Babukhiv village; highways, agricultural land, rural area, flat area
8	49.207973, 24. 704042	HLR; 1 km to the BCR dam downstream, Bovshiv village; agricultural lands, roads, rural area, impact of treated wastewater from ash dumps through discharge channel, flat terrain
9	49.127244, 24.756217	HLR; 500 m to the confluence of the tributary into the main river, Tustan village; agricultural lands, flat terrain
10	49.114268, 24.754415	Dniester River 500 m from the confluence of the tributary into the main river, Halych town; agricultural lands, hilly terrain

belongs to the eastern plains ecoregion (ecoregion N16). The type of the ecoregion is medium altitude (220–400 m above sea level); the size of the catchment area is a large river (the area of its basin is from 1000 to 10000 km^2). According to (the Water Code of Ukraine, 1995), the HLR belongs to small rivers (basin area up to 2000 km^2). Geologically, the basin has a calcareous nature (limestones, chalk, marls) (Prikhodko, 2009). The HLR valley is V-shaped in the upper part, while its lower part (the location of the BCR) is mostly trapezoidal, with a width of up to 2.6 km (Kovalchuk, 2004). A characteristic feature of the river is the presence of thick peat deposits in its valley. Their extraction for the needs of agriculture had a significant impact on the ecosystem of the river. The processes of peat formation are accompanied by hydrogen sulphide emissions (Kagalo, 2006). The flow rate in the HLR in low-water years with 75 and 95% coverage is 87,9 and 118 mln. m^3, respectively, and the flow is regulated at 36.2%. The total volume of artificial reservoirs is 54.4 mln. m^3 (including the BCR 50 mln. m^3).

The main hydrological characteristics and features of the BCR are as follows. The volume of the water body is ~ 50 mln. m^3, the area of the water mirror is 2000 ha, the average length is ~ 7.5 km, the average width is ~ 2.5 km, the average depth is 3.5 m, and maximum depth is 8 m. In the cooling reservoir, because of the constant discharge of heated waters, the conditions for the formation of special hydrochemical and hydrobiological regimes have developed. The main hydrochemical indicators of the reservoir are the average mineralization (up to 500 mg/l), the amount of dissolved oxygen (2–7 mg/l), and the turbidity (up to 500 mg/l). Water temperature regime in July is +22–24 °C; the water partially freezes at the end of January – February and sometimes in March. Water level fluctuations are up to 1 m (Burshtyn power station, nd).

Among all types of water resources, underground fresh water is the most valuable for water supply. There are 15 groundwater deposits in the HLR basin, including districts of the Ivano-Frankivsk region. Groundwater reserves in deposits amount to 10.78 mln. m^3/year, including in the Lviv and Ivano-Frankivsk regions (Kovalchuk, 2004). Groundwater horizons lie at depths from 1 to 30 m. Their chemical composition is mainly of the hydrocarbonate-sodium-calcium-magnesium type with mineralization of 0.2–0.8 g/dm^3. A characteristic feature of groundwater is the low content of trace elements such as iodine, fluorine, cobalt and molybdenum.

The features of the formation of the chemical composition and quality of water in the cooling reservoir include intensive internal water exchange, increase in water temperature, long-term transformation of the chemical composition, destabilization and reconstruction of aquatic ecosystems. For the BCR, the formation of water quality and the evolution of the initial water masses depend on the number of operating power units and the heat load. In general, in order to improve the hydrological regime of the reservoir, wastewater treatment, strengthening of banks and deepening of individual sections of the reservoir are carried out. Annually, the TPP consumes more than 2,000,000 m^3 of water, which is returned to the reservoir through a diversion channel. The water leaves the station at a higher temperature (by 8–12 °C). The level of the reservoir can be regulated with the help of a sluice, for example, during the powerful flood of 2008, water was held back.

The BCR is characterized by a high level of siltation. According to (Adamenko and Prikhodko, 2000), in 1980-s this process was characterized by intensity, and the siltation volume of the reservoir was 2.6 mln. m^3, that is, the average annual intensity was within 370,000 m^3 of sediments.

As a result of the construction of the dam, there was a rise in the groundwater level in the river valley above the reservoir and, accordingly, the waterlogging of agricultural lands in the old part of the city of Burshtyn, the villages of Nastashino, Bovshiv. Deterioration of the quality of underground drinking water, in particular organoleptic indicators (transparency, colour, smell), was observed in the settlements located below the reservoir and storage sites for solid ash and slag waste of the Burshtyn TPP in the villages of Bovshiv, Zadnistriansk, Slobidka-Bilshivtsivska and Poplavniki. Ash pits, to which TPP return water is transported together with solid waste pulp, are located on permeable peatlands without the necessary screening of the bottom, as a result of which polluted water is filtered into underground aquifers.

Surface water is used only for the technical needs of the Burshtyn TPP (reservoir-cooler) in the amount of 35,000,000 m^3/year, 2,410,000 m^3 of return water was discharged into the HLR in 2008, and the discharge of the Burshtyn TPP is 2,110,000 m^3. In 2008, the contents of iron, sulphates, nitrites, petroleum products, and organic substances in the water of the HLR in front of the BCR and in the reservoir exceeded the threshold limit value (TLV). According to (Prikhodko, 2009), after discharge of return water from slag dump N3 of the Burshtyn TPP, the water in the HLR is also contaminated with sulphates, oil products, and organic substances, but in quantities that do not exceed their concentrations in the river waters before flowing into the BCR.

Water quality in the hydrological system BCR & HLR & Dniester River in 1993–2019

Water quality in the HLR, Dniester River and BCR has been regularly studied, and the mean data on the water parameters in 1993 and in 1995–1999 are given in Table 2 and Table 3, respectively. Some water quality parameters in Tables 1–2 exceeded the TLV in several times. According to hydrobiological indicators in 2000, the water of the Dniester River was moderately polluted, and its quality was approaching the oligosaprobic type (Adamenko and Prikhodko, 2000). At the Burshtyn TPP, the repair workson the old biological treatment facilities with a capacity of 5200 m^3/year was started with the reconstruction of biofilters into aerofilters, which will make it possible to improve the quality of sewage treatment to healthy indicators. In the HLR, sulphate content exceeded 100 mg/dm^3, while in the BCR the amount of sulphate exceeded 90 mg/dm^3, the ammonium ions – 0.8 mg/dm^3, biochemical oxygen demand (BOD) – 3.3, iron ion (maximum limit 0.3 mg/dm^3), total iron in water 0.4 mg/dm^3.

In this study, the trends, regularities and interconnections between the datasets collected during the years 1993–1999 before the military activity in the region compared to the data measured on the samples collected in 2014–2024. Statistical methods are very helpful in determination of the influences of the industrial, chemical and military pollutions. Based on the regularities revealed, a more efficient strategy for the post-war restoration of the hydrological system can be elaborated and validated.

The water quality indicators in the BCR in 2015 were measured on the water samples: BOD full, chemical oxygen demand (COD), ammonium nitrogen. Taking into account the values of the indicators in 2014, we can conclude that the state of water in the BCR has not changed and is satisfactory (Ivano-Frankivsk Regional State Administration, 2015). It is almost impossible to estimate the emission of pollutants from a TPP on daily basis and because the rate of pollutant discharge from a particular TPP may vary significantly (Bera and Mahapatr, 2021).

In 2016, the indicators changed as follows compared to 2015: total BOD increased by 1.2 mgO$_2$/dm^3, which is 1.5 times higher than the TLV; COD increased by 5 mgO$_2$/dm^3, which is 1.5 times higher than the TLV; ammonium nitrogen increased by 0.8 mg/dm^3 (Ivano-Frankivsk

Table 2. Hydrochemical indicators of water quality in the HLR, Dniester River and BCR (Adamenko and Prikhodko, 2000; Prikhodko, 2009)

No.	Substance	Units	Quality indicators			
			HLR	Dniester River	BCR	TLV
1	pH	-	7.8–8.0	7.8 – 8.1	8.1–8.2	6.5–8.5
2	Dry residue	mg/dm^3	440–582	254–390	507–536	1000
3	Mineral residue	mg/dm^3	520–718	652–1042	486–661	1000
4	Oxidability, permanganate	O_3/dm^3	0.5–15.3	9.7–14.5	6.0 – 7.1	4
5	Alkalinity	mmol/m^3	3.4–5.3	2.4–3.7	4.8–4.9	3–8
6	General hardness	mg-eq/dm^3	7.9–10.9	5.0–7.5	6.0–8.0	5–8
7	Carbonate hardness	mg-eq/dm^3	3.8–5.6	2.5–4.0	2.4–3.4	–
8	Non-carbonate hardness	mg-eq/dm^3	4.1–5.3	2.5–3.5	3.6–4.6	–
9	Calcium	mg/dm^3	79.5–198	60.0–81.5	91.6–127.3	200
10	Magnesium	mg/dm^3	12.2–54.7	24.3–41.3	17.0–22.0	50
11	Sodium and potassium	mg/dm^3	2.3 – 9.2	11.8–21.4	11.6–25.3	200
12	Ammonium	mg/dm^3	0.1–2.0	0.1–3.0	0.4–0.7	0.5
13	Common iron	mg/dm^3	0.2	0.3	0.3	0.3
14	Sulfates	mg/dm^3	77.3–158.1	113.5–157.3	125.3–182.4	500
15	Chlorides	mg/dm^3	24.0–25.6	17–19	21.0–24.0	350
16	Nitrites	mg/dm^3	0.05–0.5	0.02–0.2	0.05–0.3	3.3
17	Nitrates	mgN/dm^3	1.0–5.0	3.0–6.0	2.0–6.0	45mg/l
18	Free CO_2	mg/dm^3	8.8–17.6	6.6–22.0	8.8–13.2	< 15 mmol/l*
19	Aggressive CO_2	mg/dm^3	0	< 2.2	0	> 15 mmol/l*

Note:*At minimum possible contents of Cl^- and SO_4^{2-} ions and at the minimum bicarbonate alkalinity, water is aggressive when CO_2 amount higher this value.

Table 3. Data reported on water quality at the conjugation of the HLR and the Dniester River, in 1995-1999 compared to the TLV values, in mg/dm^3 (Adamenko & Prikhodko, 2000)

No.	Year	NH_4	*BOD_5	Mineralization	Cl^-	SO_4^{2-}
1	1995	0.45	2.4	305	41	44
2	1996	0.82	3.1	425	48	88
3	1997	0.87	2.9	328	33	72
4	1998	0.51	2.6	258	24	52
5	1999	0.76	3.53	315	33.3	65
6	TLV	0.5	3.0	1000	350	500

Regional State Administration, 2016). Therefore, the water of the BCR can be estimated as the III-rd quality class of 4 categories, and as "satisfactory" according to their condition, and as "slightly polluted" according to the degree of purity.

During 2017 there was a tendency towards a slight increase in the average concentrations of pollutants. Thus, in the control plant in Halych, the average value of the indicator BOD during this period increased by 1.0 mgO_2/dm^3, value of the indicator of COD increased by 11 mgO_2/dm^3 (Ivano-Frankivsk Regional State Administration, 2017). According to the Methodology for ecological assessment of the quality of surface water, in all observation sites along the Dniester River the water can be estimated as the III-rd quality class according to 4 categories, and according to their condition is "satisfactory", and according to the degree of purity is "slightly polluted". The water quality indicators in the BCR changed in 2017 we can conclude that the water condition according to the ecological classification, the waters in the reservoir belong to the II quality class, category 3 and according to their condition – "good", according to the degree of purity – “fair” clean” (State Agency of Water Resources, 2017).

In 2018, a significant anthropogenic load on the tributaries of the Dniester River was detected. The water quality in some of them has deteriorated is due to abnormally high temperature during the summer months: the increase in the content of ammonium ions, iron, salts and organic pollution, and by a decrease in the content of oxygen dissolved in the water. The water in the Dniester River was estimated as the III-rd quality class, 4-th category, and according to their condition as “satisfactory”, and according to the degree of purity as “slightly polluted”. The water in the BCR were of the III-rd quality class, 4 categories, and according to their condition are “satisfactory”, according to the degree purity are “slightly polluted” (Ivano-Frankivsk Regional State Administration, 2018).

In 2019, seven toxic organic substances in the water samples from the Dniester basin were found, namely: hexachlorocyclohexane, DDT, hexachlorobenzene (insecticide), fluoranthene, naphthalene; trichloromethane, and tetrachloromethane. The content of the detected pollutants did not exceed the annual average and maximum permissible concentrations of environmental quality standards ENYAsr and ENYAmax. According to the results of these studies, a good chemical state of the surface water bodies in all monitoring points was established. The results of radiological studies showed that in the studied samples no excess of cesium-137 and strontium-90 content above the established permissible levels of radionuclide content was found (Ivano-Frankivsk Regional State Administration, 2019).

Own measurements of pollution contents in the hydrological system in 2020–2024

In 2020, a diagnostic monitoring was carried out in accordance with the programs approved by the State Water Agency order No. 21 dated 11.01.2020 and order No. 587 dated 24.06.2020, which established 20 points on the territory of Ivano-Frankivsk region; namely, 15 in the Dniester river basin and 5 in the Prut river sub-basin. It was established that the left and right banks of the BCR are subject to different technogenic loads, different parts of the reservoir are subject to different levels of influence from different sources of pollution and, as a result, have different water quality classes (Rychak and Arkhypova, 2024). It is necessary to continue monitoring studies to increase the level of environmental safety of water bodies within the influence of the TPP in terms of increasing control structures. For more detailed analyses of water quality in the BCR and the rivers in its vicinity ten water samples were taken from the locations marked on the map (Figure 1) during the fall of 2023 and 2024 and spring 2024.

Laboratory studies were carried out in the educational and research laboratory of analytical ecological studies of the Scientific Institute of Ecology of V.N. Karazin Kharkiv National University (KhNU), Kharkiv, Ukraine and measurement of the content of chemical compounds in 2023 and 2024 in the laboratory control department of the Municipal Enterprise “Ivano-Frankivskvodoekotechprom” Ivano-Frankivsk city, Ivano-Frankivsk region, Ukraine. The department is certified for the right to perform measurements (Certificate of Technical Competence No. IF – 402 dated 06/13/2022 issued by the State Enterprise “Ivano-Frankivsk Center for Standardization, Metrology and Certification”. The measurements were carried out in accordance with the measurement methods approved for use (appendix to the certificate).

The prerequisite for determining these components is that they are the main hydrochemical elements that determine the direction of hydrochemical processes in heated waters and negatively affect the technological processes associated with the operation of the heat exchange equipment of the enterprise, as it is substantiated in (Romas, 2002).

RESULTS OF STATISTICAL ANALYSIS

In the water samples taken from the HLR in front of the BCR exceeding environmental standards for nitrites and sulphates were detected. In the water sample taken near the return water discharge of the slag pit, an elevated level of sulphates was also noted (Table 4), but their amounts did not exceed ones in the river waters before its fall into the BCR. For comparison reason, the water parameters in the reservoir in autumn 2024 are given in Table 4.

The data given in Tables 2–4 have been treated by statistical methods including the descriptive statistics and correlation analysis. The results are presented in relative values computed as ratios of the measured value and the TLV

Table 4. Content of pollutants (mol/dm^3) in the BCR and the HLR at the sites 1–6 (Figure 1)

Date	October 23, 2023							October–December 2024			
N	Substance	Sample 1	Sample 2	Sample 3	Sample 4	Sample 5	Sample 6	Samples 1-5 (mean value)	Sample 6	Sample 8	TLV
1	pH	7.892	7.624	7.573	7.668	7.775	7.775	7.2	7.1	6.8	6.5–8.5
2	Alkalinity	3.5	3.1	3.3	3.6	4.2	4.2	5.3	4.5	4.3	3–8
3	Chlorides	17.90	21.88	21.84	17.9	18.2	18.2	26.5	20.4	22.9	350
4	Suspended substances	22.0	74.0	28.0	40.0	2.0	2.0	-	-	-	30
5	Dry residue	410.6	359.0	396.2	398.7	310.0	310.0	392	497	376	1000
6	Rigidity	6.4	6.6	6.5	7.0	7.0	8.0	5.51	6.13	6.04	5–8
7	Sulfates	104.2	128.4	124.0	121.5	121.4	91.4	81.4	93.1	97	500
8	Ca	100	93	96	98	101	100	103.1	181.17	103.2	200
9	Mg	15	16	17	16	19	-	17.03	17.23	17.05	50
10	K	20	18	16	16	14	15	18.72	5.32	6.54	20
11	Na	10	11	12	8	9	14	14.83	13.27	19.75	200
12	Ammonia	-	-	-	-	-	-	0.1	0.2	0.008	2.0
13	Smell	-	-	-	-	-	-	2	0	0	> 2
14	Transparency	-	-	-	-	-	-	0.25	0.25	0.25	0.5–2
15	Turbidity	-	-	-	-	-	-	1.75	1.5	1.5	5–25
16	Nitrites	-	-	-	-	-	-	0.003	0.003	0.002	3.3
17	Nitrates	-	-	-	-	-	-	3.8	4.4	3.2	45
18	Fe	-	-	-	-	-	-	0.004	0.002	0.002	0.3
19	Zn	-	-	-	-	-	-	0.006	0.006	0.005	1.0
20	Cu	-	-	-	-	-	-	0.001	0	0	1.0
21	Mn	-	-	-	-	-	-	0.002	0.002	0.001	0.1
22	Cd	-	-	-	-	-	-	0.001	0.001	0.001	0.001
23	Cr^{6+}	-	-	-	-	-	-	0.001	0.001	0.001	0.05
24	Sr	1.5	1.4	1.2	1.3	1.2	1.4	1.25	2.27	1.44	7.0

value of the corresponding pollutant. Therefore, all the values in the diagrams below are non-dimensional concentrations C_j of the corresponding pollutants j = 1, 2, …, n relative to their TLV values. In the year 1993, most of the water parameters in the cites 4, 6, 10 were well below of their TLV values (i.e. < 1 in Figure 2), except for the Cl^-, general hardness and oxidation (measured by permanganate). It means, the pollutions and their combinations responsible for the high level of oxidation, pH and free CO_2 were transferred from the HLR (site 6) and the BCR (site 4) to the Dniester River (site 10). Nevertheless, the levels of Cl^-, general and non-carbonate hardness were lower in the sample 10 compared to the same levels in the samples 4 and 6, that confirms accumulation of these pollutants in the BCR and the HLR along the distance between the sites 8 and 9 (Figure 1). The cites 4, 5, 10 were chosen for presentation in Figure 2 because the datasets for n = 19 water characteristics are present in the open sources only for these cites (Prikhodko, 2009).

The commonly used index BOD that shows the amount of oxygen consumed by bacteria and other microorganisms while they decompose organic matter under aerobic conditions at a given temperature, slightly exceeded the TLV values in dynamics during the years 1995–1999 even in the Dniester river (sample 10), as it is shown in Figure 3. Other parameters as ammonia, Cl^- and SO_4^{2-} ions, and total mineralization were well below the maximal TLV values (Figure 3). Unfortunately, in 1990-1999 less attention paid to systematic monitoring of water quality with a complete set of hydrochemical parameters due to economic and political changes in the Ukraine. Therefore, only five water characteristics only for the cite 10 have been found in the open sources.

A comparative analysis of the water parameters in the samples 4 and 10 collected in the years

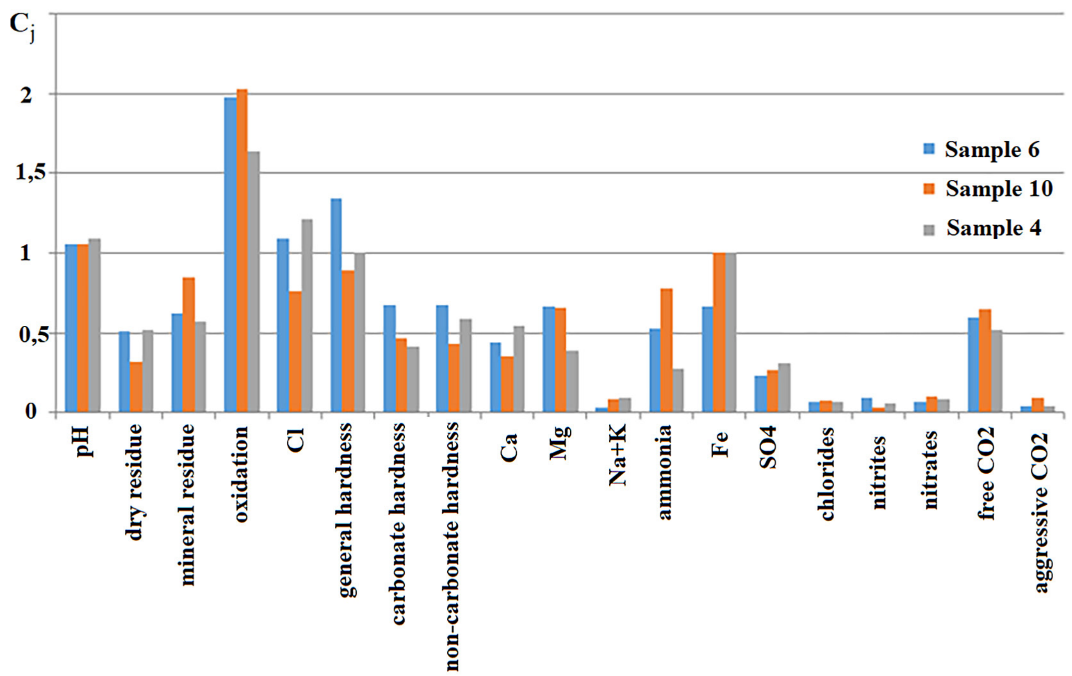

Figure 2. Mean values of the hydrochemical water parameters C_j, j = 1, 2, …, 19 (relative to their TLVs) in the sites 4, 6, 10 in 1993

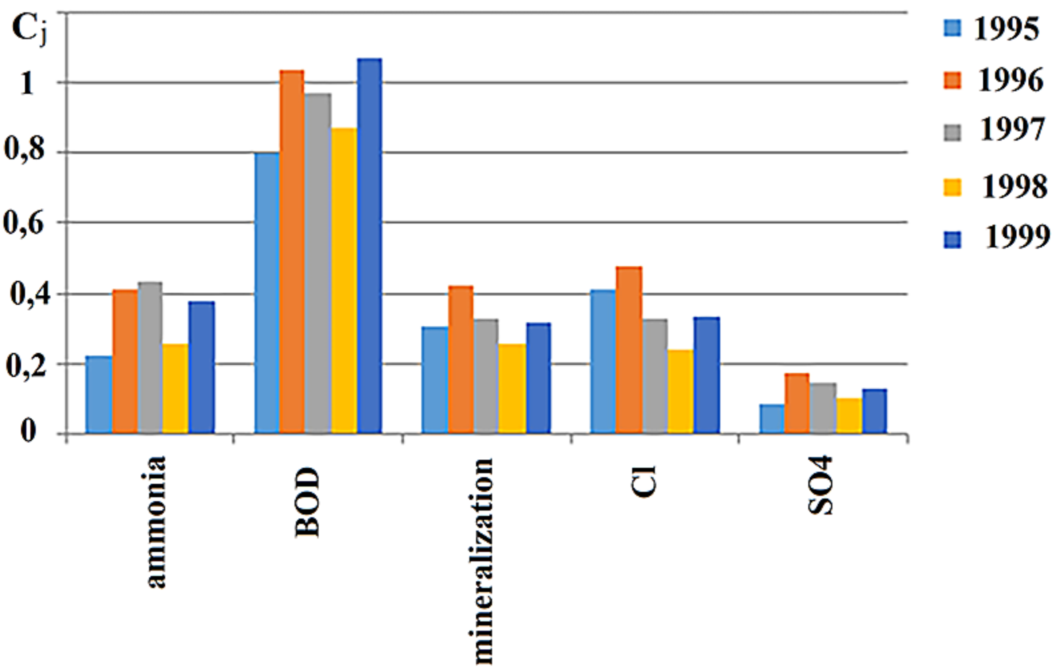

Figure 3. Mean values of some water parameters C_j, j = 1, 2, …, 5 (relative to their TLVs) in the sample10 in 1995–1999

2016-2018 revealed certain correlations (Figure 4a, b). In 2010th more attention was paid to systematic control of water quality in the hydrological system at consideration. Water characteristics n = 13 were measured and published in the open sources, namely, for 2014–2018 years in the cite 4 (Figure 4a), and for 2016–2018 years in the cite 10 (Figure 4b).

The statistical results confirm a deep interconnection of the two water bodies with the important role of the length 8–9 of the HLR as a damper. This length promotes sedimentation,

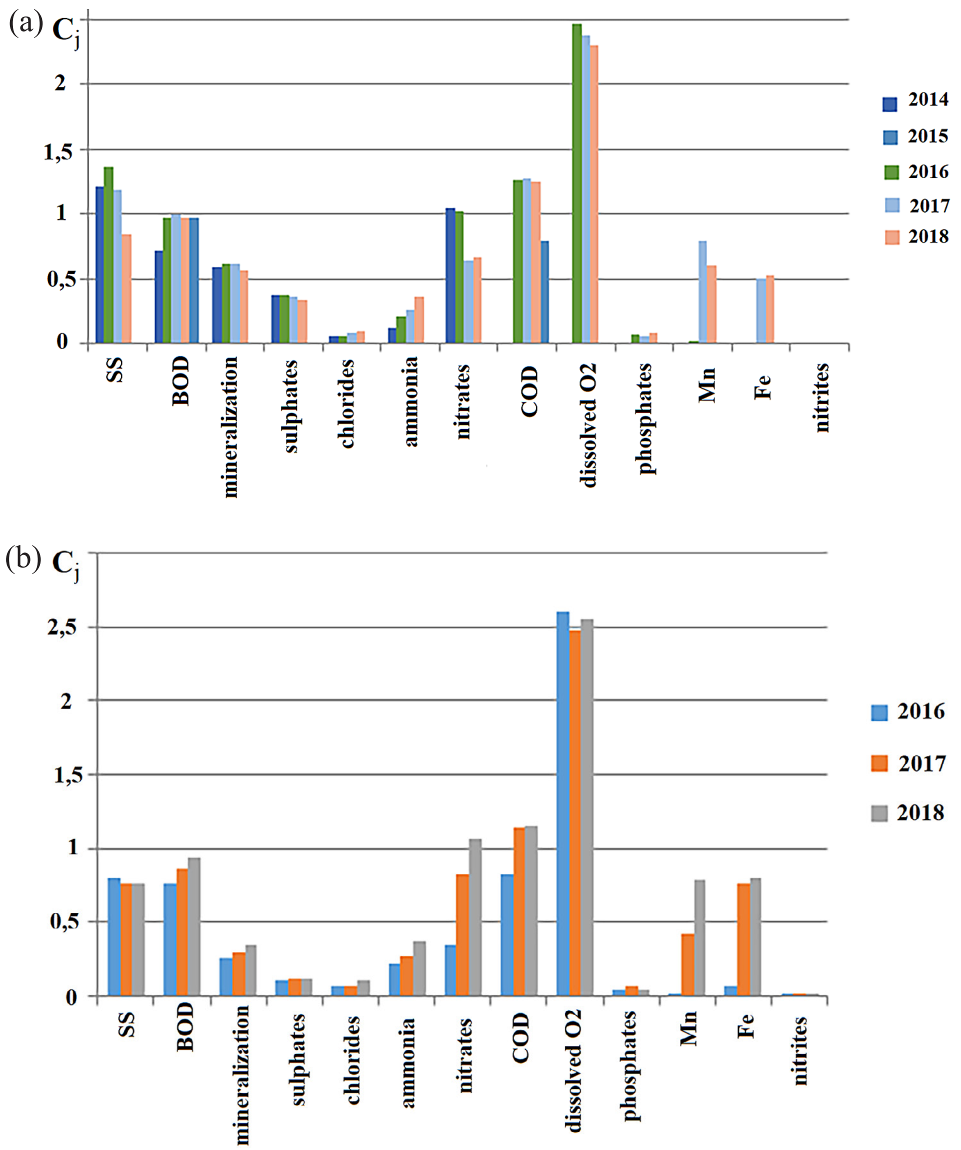

Figure 4. Mean values of some water parameters C_j, j = 1, 2, …, 13 (relative to their TLVs) at the site 4 in the 2014–2018 years (a), and at the site 10 in the 2016-2018 years (b)

absorption and partial self-restoration of the waters coming into the Dniester River from the BCR. The levels of all the water parameters are higher in the BCR compared to the Dniester River. In the sample 10 only the dissolved CO_2 essentially exceeds the TLV value. Two more parameters as nitrates and the COD are slightly larger the TLV values. Here COD is an important indicative measure of the amount of O_2 that is consumed by chemical/biochemical reactions at given temperature. Therefore, the increased BOD and COD indexes could point out either the worse water quality or the raised mean temperature due to the global climate warming.

The results of correlation analysis of the water parameters C_j, j = 1, 2, …, 13 presented in Figure 4a, b are given in Figure 5. It revealed a reliable correlation (Table 5) between all n = 13 water characteristics presented in Figure 4a, b for the 2016–2018 years because the common data between the cites 4 and 10 exists for the 2016–2018 years only. The linear correlation gives rather good dependences with reliability coefficients R^2 > 0.87 that pointed out a functional dependence between the water parameters in the samples 4 and 10. The tangents in the linear approximations of the trend lines (Table 5) increases with years from 2016 to 2018 that point out a graduate exhaustion of the water system for the self-restoration process. A better approximation between the water parameters in the two interconnected water bodies is described by the polynomial functions

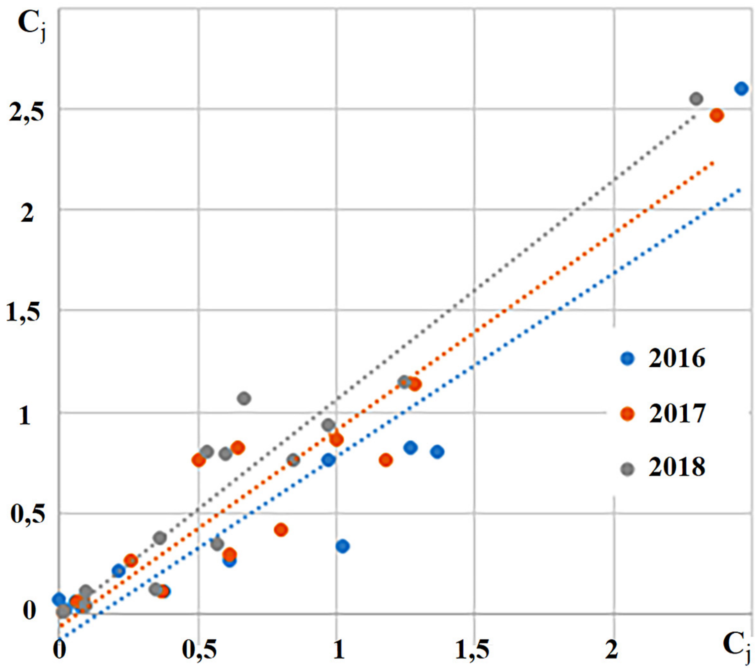

Figure 5. Statistical dependencies between the non-dimensional hydrochemical parameters of water C_j, j = 1, 2, …, 13 presented in Figures 4a, b in the BCR (sample 4, horizontal axis) and the Dniester River (sample 10, vertical axis)

of the second order (Table 5). The data presented in Figure 5 and Table 5 confirmed an existence of the functional dependence between all the water parameters (n = 13) that can only be explained by the flows between the two water bodies and sedimentation & absorption processes in the length 8–9 of the HLR as a damper in this system.

The water parameters in the samples collected in October 2021 (own data samples) confirm (Table 3) higher pressure onto the water system near Burshtyn TPP (Figure 6). Here n = 11 hydrochemical parameters have been evaluated in six samples. The values of pH and rigidity are close to the TLV limits. The alkalinity exceeds this value in ~ 2 times, while the suspended substances exceeds the TLV in > 2 times. This is the outcome of accumulation of the military pollutions near the TPP. The latest data on the samples collected in 2024 in the cites 6, 8, and in the BCR (mean value based on the samples 1–5) are given in Figure 7. Existence of the high pressure onto the water system near the BCR is confirmed by the pH value, general hardness and the level of some heavy metals (Cd). The values of alkalinity still exceed the TLV in > 2 times.

RESULTS OF LABORATORY ANALYSIS

The BCR was created for a circulating technical water supply system. In the process of using water to cool the TPP units, the temperature of the discharged water into the drainage channel increases by 8–12 °C (Burshtyn power station), which affects the course of physicochemical processes in BCR. Due to the increase in water temperature and the acceleration of the course of many chemical processes, the chemical composition of the water changes, which in the case of water from the BCR increases the specific gravity

Table 5. Regression dependencies revealed by statistical analysis of the data presented in Figure 4a, b

Year	Linear regression		Parabolic regression	
	Function	R^2	Function	R^2
2016	y = 0.9088x - 0.131	0.8731	$y = 0.3802x^2 + 0.088x + 0.0634$	0.9754
2017	y = 0.9749x - 0.0687	0.8999	$y = 0.1865x^2 + 0.565x + 0.0551$	0.9220
2018	y = 1.0887x - 0.0271	0.9288	$y = 0.0397x^2 + 1.0011x$	0.9296

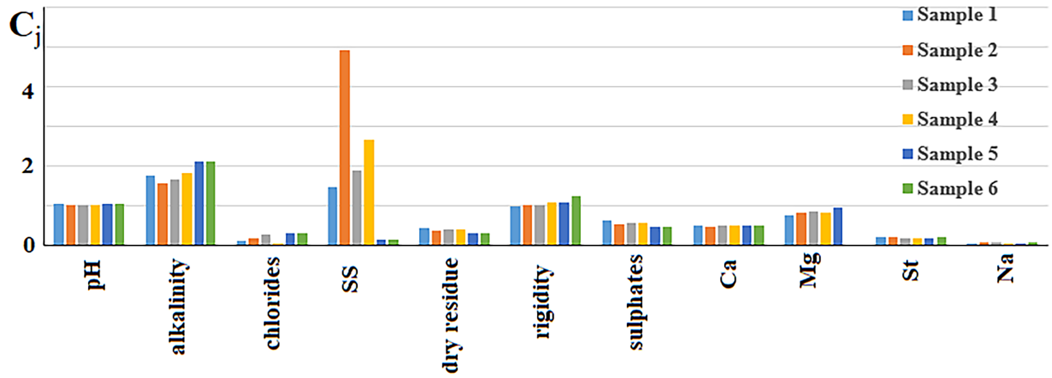

Figure 6. Mean values of the water parameters (relative to their TLV) from Table 3

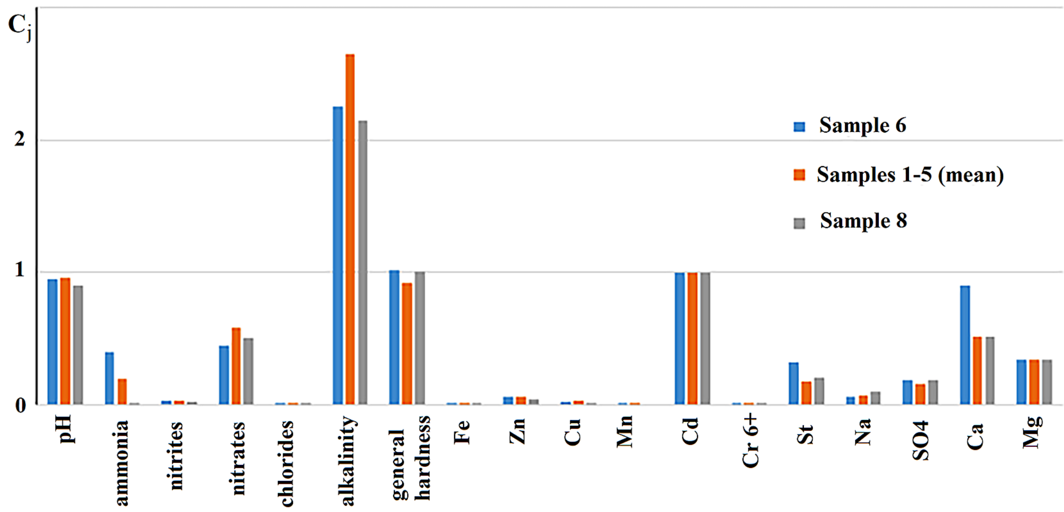

Figure 7. Mean values of the water parameters C_j, j = 1, 2, …, 18 (relative to their TLV) from Table 4

of calcium and magnesium carbonate compounds (Romanenko, 2001). According to the results obtained over 30 years (1993–2023), Tables 2–4, the calcium content (site 6) increased by 30 % (from 138 mg/dm^3 to 181 mg/dm^3); in the BCR, there is a tendency to reduce the content of Ca^{2+} (from 91–127 mg/dm^3 to 82 mg/dm^3); at site 9 (Dniester River) the calcium content was (60–80 mg/dm^3, 1993), at site 8 (HLR) a decrease in the content is observed (to 109 mg/dm^3). In general, except for the section to the reservoir, a tendency to increase the calcium content is observed, in the reservoir and on the section of the HLR from the reservoir to the Dniester River, a tendency to decrease the calcium content is observed.

Let's consider the situation with the magnesium content. In 1993, the content of Mg^{2+} cations ranged from 12 to 54 mg/dm^3 (Table 2), at the current stage of the study the content is < 19 mg/dm^3 (Table 4). It is difficult to determine the trends in the behavior of cations; regarding the content in the reservoir waters. There is a slight tendency to decrease (from 17 mg/dm^3 to 22 mg/dm^3 to an average value of 17 mg/dm^3) (Tables 2–4), however, it is possible to hypothesize a stable Mg^{2+} content in the artificial water system (according to the results of detailed studies of the content of Mg^{2+} cations at different sites of the BCR in 2023 and 2024) (Table 4). We observe the depletion of the water system at the sites of the HLR and of the Dniester River (sites 8 and 9). The content of Mg^{2+} cations decreased to 17 mg/dm^3 from 2023 to 2024 (Table 4). In general, we can state that at the current stage of the study, a stable content of Mg^{2+} cations was observed in the hydrological system, but in the spatio-temporal section, depletion of the natural component of the system HLR – Dniester River was observed, and the artificial system BCR, under human control, ensures the stability of the required amount of Mg^{2+} cations.

In the cooling reservoirs with a circulating system, the total mineralization increases. After passing through the heat exchange systems of power plants, water loses a certain amount of salts, and its total mineralization decreases (Romanenko, 2001, Romas, 2002). The initial data for the study were the results of a chemical analysis in 1993, where the mineral residue and dry residue were studied. As a result of comparing the indicators, a significant content of mineral residue was noted, which indicates the predominance of inorganic substances in the water in all areas of the study of the natural-artificial hydrological system: the predominance of mineral residue in the waters of the HLR is up to 100 mg/dm^3 (site 6), in the waters of the Dniester River up to 520 mg/dm^3 (site 10), in the reservoir the content of organic and mineral residue is almost the same and the difference between the indicators is up to 50 mg/dm^3. In the spatiotemporal section, the mineralization content indicators are variable: changes of ±100 mg/dm^3 were observed (Table 3, in absolute values) with a tendency to increase in recent years by an average of 10–12 mg/dm^3 (Table 4).

Now we analyse the changes in the water hardness indicators in the natural-artificial hydrological system considered. The average water hardness indicators for the HLR (site 6) in 1993 were 7.9–10.9 mg-eq/dm^3 (Table 2); in 2024 it was 6.13 mg-eq/dm^3 (Table 4). In the Dniester River (site 10), the hardness indicator was 5–7 mg-eq/dm^3 in 1993 (Table 2), and today in the HLR (the sires between 8–10), the hardness is 5.51 mg-eq/dm^3 (Table 4). Therefore, we observe a tendency to reduce the hardness of natural waters. Note, that the indicators differ quite a bit, however, in general, according to the hardness classification, these natural waters belong to hard waters. They flow through limestone rocks and the natural content of Ca^{2+} and Mg^{2+} also creates conditions for increasing water hardness. Regarding the waters in the reservoir, we observe a stable finding of hardness indicators within 6–8 mg-eq/dm^3 (hard water) with unstable variability. Compared to the hardness indicators in other cooling reservoirs, for example, after several years of operation of the Chernobyl NPP, the total mineralization of water in the cooling reservoir increased from 244 to 280 mg/dm^3, and the hardness increased from 2.7 to 2.9 mg-eq/l (Romanenko, 2001). Such changes occur mainly as a result of water evaporation. In the waters of the BCR, the indicators are much higher, which indicates a significant contribution of natural factors in the formation of water quality.

With increased alkalinity, which was observed in natural waters (Figure 7), they have the ability to better resist changes in acidity. Low alkalinity makes water more vulnerable to anthropogenic load. Regarding the artificial water reservoirs, in the hydrological system of HLR & BCR & Dniester River, if the alkalinity of the water is < 50 mg/l in terms of $CaCO_3$, the water will be aggressive, which will cause corrosion of any metal surfaces in it. Alkalinity is formed by hydrocarbonates (HCO_3^-), carbonates (CO_3^{2-}, at higher pH). In the natural waters of Rohatyn Opillia, the main source of alkalinity is Ca and Mg bicarbonates, which enter the water as a result of the dissolution of limestone ($CaCO_3$) or other carbonate rocks. According to the results of our research, a close correlation was established between alkalinity and the content of Ca^{2+} and Mg^{2+}, because in natural waters they form carbonate equilibriums.

The quality of water in rivers and reservoirs is significantly affected by the spatial correlation between anthropogenically transformed (eco-negative) and natural (eco-positive) subsystems of the landscape within the geosystems of catchment basins. An increase in the share of eco-negative areas leads to an intensification of pollutant flows into water bodies and deterioration of their ecological condition (Rychak et al., 2024). The study of spatial and temporal changes in the structure of basins and their impact on water quality will allow us to better understand the ability of water bodies to self-regulate and resist anthropogenic and anthropogenic loads.

CONCLUSIONS

The study highlights key aspects of the environmental impact of the Burshtyn TPP, the largest in the western region of Ukraine. Reasoned conclusions are presented based on the analysis of archival data on the quality of surface waters within the impact of the man-made object and the data obtained from field research in modern conditions. The scientific novelty of the conducted research lies in the fact that the work complements existing knowledge in the field of environmental safety of surface water bodies within the long-term impact of man-made loads.

Therefore, slow but monotonous dynamics in the changes of water quality in the connected hydrological system HLR & BCR & Dniester River during the last 30 years of a hydrochemical load by the Burshtyn TPP, has been confirmed by a detailed statistical analysis of the data available from the open sources. During the spatial-temporal period of the study, an analysis of the content of heavy metals in the natural-artificial hydrological system was also conducted. When atmospheric air is polluted as a result of the operation of a TPP, according to our research, in the surface waters of the HLR, the Dniester River, and the BCR there are only traces of Zn, Co, Mn, and Cr. At the level of 0.5 – 1 TLV was recorded for the content of total Fe and Cd.

Statistically significant relationships between water parameters in the BCR and the transboundary Dniester River were obtained. The practical significance of the results obtained lies in the created basis for further modeling and forecasting of the anthropogenic load of TPP on their cooling reservoirs and associated watercourses of subsequent orders.

Our further research will focus on conducting a chemical analysis to determine the content of heavy metals in the bottom sediments of the reservoir and rivers, aiming to detect long-term changes resulting from the influence of the TPP.

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